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Electron spin resonance studies of Co(tbp)·C_{60} single crystal

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Abstract

ESR measurements have been made on a newly synthesized cocrystallite of C_{60} with the Co^{II} complex of 5, 10, 15, 20-tetrakis[3, 5-(di-*tert*-butyl)-phenyl]porphyrin (tbp) single crystal to study the strong intermolecular interactions which are suggested by x-ray structural analyses. A single anisotropic ESR absorption line is observed at room temperature with the principal g-values $g_\perp = 2.423$ and $g_\parallel = 2.005$, which are typical values for the low-spin Co^{II} ions ($S = 1/2$). The antiferromagnetic superexchange interaction between Co^{II} ions via C_{60} is confirmed from the observation of the finite Weiss temperature, which is further supported by the absence of the hyperfine splitting due to ^{59}Co ($I = 7/2$) nuclei. As the temperature is lowered, the $g_\perp$-value decreases monotonically suggesting an increase of the crystal-field splitting energy. This result is consistent with the fact that the intermolecular distance between Co^{II} and C_{60} becomes shorter as the temperature decreases. The peak-to-peak ESR linewidths ΔH_{pp} along both principal axes increase with temperature due to the shorter spin–lattice relaxation time.

1. Introduction

Because the fullerene C_{60} shows a wide variety of physical properties [1–3], many kinds of material which contain C_{60} have been synthesized and extensively investigated. In addition, C_{60} is also expected to become a uniquely valuable building block in supramolecular construction. On the other hand, it is known that the round shape of C_{60} is not appropriate for cocrystallizing with planar molecules and it is necessary to form a concave surface to fit C_{60}. Recently, Co, Zn and Fe complexes of octaethylporphyrin (oep) cocrystallite with C_{60} have been found to form solids with a remarkably close contact between the curved π-surface of the C_{60} with the

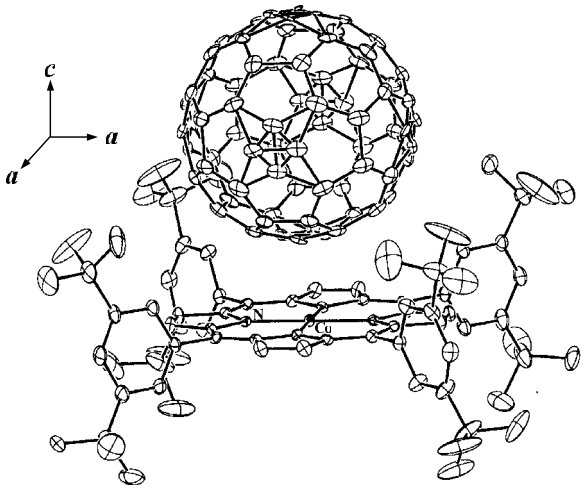

Figure 1. A view of the structural unit of $Co^{II}(tbp)\cdot C_{60}$ determined by room temperature x-ray analysis [8].

planar π-surface of the porphyrin, without the need for matching a convex with a concave surface [4, 5]. In addition, it has been found that the carbon cages of fullerenes are, unusually, not disordered in some of these cocrystallites, due to the intermolecular interaction between fullerene and the metal–(oep) complex [4]. Very recently, such metal–(oep) cocrystallites with C_{60} have been extensively synthesized and characterized by using Pd [6], Cu [6], Ag [7] and Ni [7] as the metals of *anti*-formed metal–(oep) complexes.

In this paper we report on the ESR spectra of the newly synthesized Co^{II} complex of 5, 10, 15, 20-tetrakis(3, 5-(di-*tert*-butyl)-phenyl)porphyrin (tbp) cocrystallized with C_{60}. In this material, three significant characters of the strong intermolecular interaction between the $Co^{II}(tbp)$ molecule and C_{60} have been revealed by x-ray structural analyses [8]. Firstly, it is found that the free rotation of the C_{60} molecule is suppressed and thus the absolute positions of the carbon atoms on the C_{60} are completely determined even at room temperature. In the cocrystallites with the fullerene containing the most porphyrin, it has been necessary to lower the temperature to determine the complete structure to avoid the disorder caused by the rotation of the fullerene molecule. This characteristic feature of $Co^{II}(tbp)\cdot C_{60}$ is due to the tight three-dimensional packing between C_{60} and Co^{II} porphyrin with four di-*tert*-butylphenyl groups (see figure 1). Secondly, a quite short distance has been observed between a Co^{II} ion and a carbon atom on C_{60} (2.61 Å at 293 K) and it decreases with temperature (2.58 Å at 83 K). Such close contact makes possible covalent bonding between them. Lastly, C_4 symmetrical disorder of the carbon atoms on C_{60} is observed, although each isolated C_{60} molecule does not itself possess C_4 symmetry. This unusual C_4 symmetry of C_{60} in this material is attributable to the effect of the $Co^{II}(tbp)$ molecule, which has C_4 symmetry.

Since each structural unit of $Co^{II}(tbp)\cdot C_{60}$ has a magnetic Co^{II} ion, ESR spectroscopy is a powerful tool for clarifying the variation of the intermolecular interaction between $Co^{II}(tbp)$ and C_{60}, as well as that between the $Co^{II}(tbp)$ molecules via the bulky C_{60} molecules in this system. In view of this, we report herein the temperature dependence of the ESR spectra and discuss the variation of the g-values and linewidths, as well as the spin susceptibility in this system. Some of the ESR data were briefly presented in our earlier paper, together with the x-ray structural analyses [8].

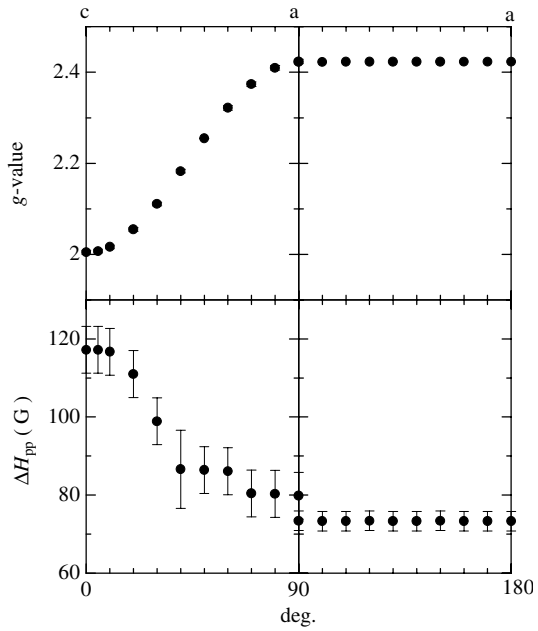

Figure 2. The angular dependence of the g-value and ΔH_{pp} for Co^{II}(tbp)·C_{60} obtained at room temperature.

2. Experimental procedure

The Co^{II}(tbp) molecule has been synthesized by modifying the terminal phenyl ligand of tetraphenylporphyrin (tpp) into di-*tert*-butylphenyl groups. The single-crystalline sample of Co^{II}(tbp)·C_{60} has been synthesized by the evaporation of a mixture of a solution of the fullerene in toluene and a solution of the Co^{II}(tbp) in toluene as described elsewhere [8]. ESR measurements were performed by using a Bruker E500 X-band spectrometer equipped with a gas-flow-type cryostat, Oxford ESR-900. Sample temperature was controlled by an Oxford ITC 601. The absolute magnitude of the spin susceptibility and g-value were calibrated using $CuSO_4·5H_2O$ and diphenylpicrylhydrazyl (DPPH) as the standard, respectively. The single-crystalline sample was mounted on a Teflon sample holder using normal silicon grease.

3. Experimental results and discussion

Figure 1 shows a view of the structural unit of Co^{II}(tbp)·C_{60} determined at room temperature. This complex crystallizes in the tetragonal space group I (no 79), with cell dimensions at room temperature of $a = 20.399(2)$ Å, $c = 12.0635(8)$ Å and $V = 5020.1(6)$ Å^3. The detailed crystal data and three-dimensional packing of Co^{II}(tbp)·C_{60} are presented in table 1, figure 3 and figure 4 in [8]. The Co^{II}(tbp) is positioned symmetrically between two fullerene units along the c-direction and the closest contact between the fullerene and the atoms of the Co^{II}(tbp) is achieved in this direction (2.61 Å at room temperature). The fullerene is 'caught' by two porphyrin planes, from top and bottom in the c-direction, and, further, surrounded by four porphyrins placed side by side in the aa-plane. The fullerene is located in the position of closest approach to the centred cobalt ion, which involves an electron-rich π-bonding 6:6 carbon ring junction (hexagon–hexagon junction).

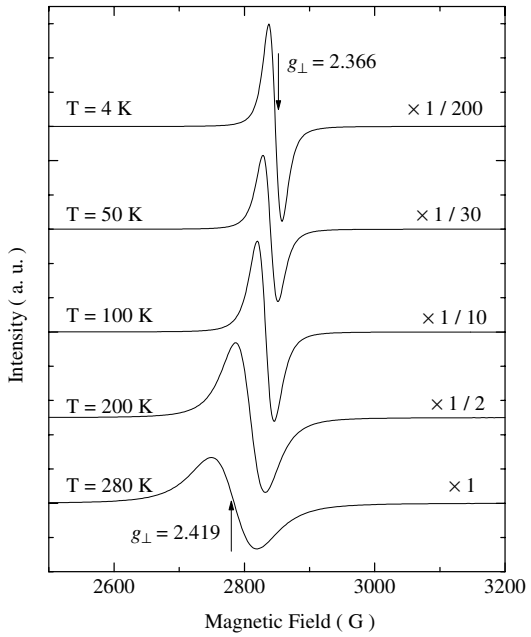

Figure 3. Temperature variation of the first-derivative ESR spectra with the magnetic field $\boldsymbol{H}$ within the aa-plane. The g-values are determined from the zero-intensity field represented by the arrows.

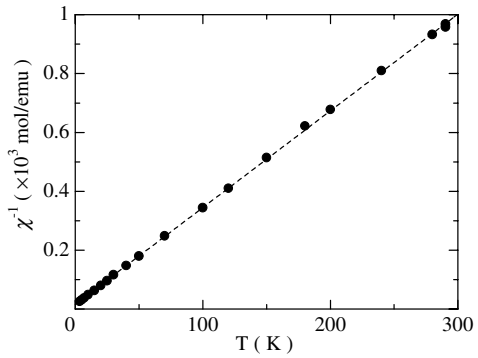

Figure 4. Temperature dependence of the inverse spin susceptibility χ^{-1} of $Co^{II}(tbp)\cdot C_{60}$ with the magnetic field $\boldsymbol{H}$ within the aa-plane. The dashed line represents the fitting by the Curie–Weiss law.

The magnetic Co^{II} ion is placed in the tetragonal crystal field consisting of four-coordinated nitrogen atoms of the porphyrin molecule and the carbon atoms of the fullerenes. Figure 2 shows the angular dependence of the g-value and peak-to-peak ESR linewidth ΔH_{pp} of $Co^{II}(tbp)\cdot C_{60}$ with the external magnetic field $\boldsymbol{H}$ within the ac- and aa-planes at room temperature. Both the g-values and ΔH_{pp} show uniaxial anisotropy reflected in the tetragonal symmetry of the crystal field, i.e., a large variation in the ac-plane but almost no change in the aa-plane. The principal g-values are obtained as $g_\perp(\boldsymbol{H} \parallel aa\text{-plane}) = 2.423$ and $g_\parallel(\boldsymbol{H} \parallel c\text{-axis}) = 2.005$ at room temperature. These values are typical for the low-spin Co^{II} ions where the unpaired electron resides on the $Co(3d_{z^2})$ orbital. In fact, crystal-field theory predicts the following relation for this electron ground state [9]:

$$g_\perp = g_e - 6\left(\frac{\zeta}{\Delta E}\right), \qquad g_\parallel = g_e, \tag{1}$$

where g_e, ζ and ΔE represent the free-electron g-value (2.0023), the spin–orbit coupling constant ($\zeta < 0$ for the d^7 configuration) and the energy of the crystal-field splitting between d_{z^2} and d_{xz}, d_{yz} orbitals, respectively. This equation clearly explains the observed anisotropy of the g-values. Here, we should note that the $g_\parallel$-value obtained is slightly larger than the theoretical expectation. This discrepancy is often observed for square-planar Co^{II} complexes and is attributable to the small mixing of the $d_{x^2-y^2}$ orbital into the ground-state d_{z^2} orbital [10].

Figure 3 shows the temperature dependence of the ESR spectra for $\boldsymbol{H}$ within the aa-plane, together with the definition of the g-value. A nearly Lorentzian-shaped ESR absorption line is observed for the whole temperature region at every direction of $\boldsymbol{H}$ and no hyperfine splittings were resolved due to the ^{59}Co nuclei (natural abundance of 100%, $I = 7/2$). This indicates that hyperfine splitting in this material is averaged out due to the exchange interaction between Co^{II} ions, as discussed later. Furthermore, no ESR lines were observed around $g \sim 1.999$, which correspond to the absorption by the C_{60}^- radical [11]. This indicates that no charge transfers between molecules have occurred in this material, such as $[Co^{II}(tbp) + C_{60} \rightarrow Co^{III}(tbp) + C_{60}^-]$.

Figure 4 shows the temperature dependence of the inverse spin susceptibility χ^{-1} for $\boldsymbol{H}$ within the aa-plane. The dashed line represents the fitting by the Curie–Weiss law. The spin susceptibility along the c-axis showed almost the same tendency as that along the aa-plane. As can be seen in this figure, χ follows the Curie–Weiss law, $\chi = C/(T + \theta)$, with the finite antiferromagnetic Weiss temperature θ. The estimated value of θ is about 4.9 K. The non-zero value of θ suggests that there is a finite superexchange interaction between Co^{II} ions via the C_{60} molecule along the c-axis, although the Co^{II}–Co^{II} distance itself is rather large: 12.0635(8) Å at room temperature. This result reflects the close packing between the Co^{II}(tbp) and C_{60} molecules in this direction, i.e., the wavefunctions of the d_{z^2} orbital of the Co^{II} ion and the curved π-orbital of the fullerene overlap considerably with each other.

To obtain the temperature variation of the intermolecular interaction between the Co^{II}(tbp) and C_{60}, we plot the principal g-values of Co^{II}(tbp)·C_{60} in figures 5(a) ($g_\perp$) and (b) ($g_\parallel$). Since the wavefunction of the Co($3d_{z^2}$) orbital, on which the unpaired electron resides, is considered to be sensitive to the location of the C_{60} molecules along the c-direction, these parameters act as sensitive probes of the intermolecular interaction in this material. As shown in figure 5(a), the characteristic behaviour of the $g_\perp$-value is revealed, i.e., it decreases monotonically with temperature, whereas the $g_\parallel$-value in figure 5(b) is almost unchanged. This decreasing $g_\perp$-value directly indicates that the intermolecular interaction increases in the low-temperature region as discussed below. As shown in equation (1), the $g_\perp$-value shifts by $6(\zeta/\Delta E)$ from g_e. Thus the observed decrease of the $g_\perp$-value indicates the increase of the energy separation ΔE at low temperature. In other words, the Co($3d_{z^2}$) orbital is destabilized as the temperature is lowered. Such behaviour is expected in the case where the intermolecular distance between Co^{II}(tbp) and C_{60} along the c-direction is decreasing with temperature. This result agrees excellently with the results of the x-ray structural analyses, which suggest that the interatomic distance between the Co^{II} ion and the carbon atom on C_{60} decreases from 2.61 Å at 293 K to 2.58 Å at 83 K along the c-direction [8]. Figure 5(a) further suggests that even shorter contacts should be achieved between the molecules at temperatures below 83 K. On the other hand, equation (1) predicts constant $g_\parallel$-values of g_e—which is actually observed, as shown in figure 5(b)—although the value increases slightly in the low-temperature region of $T < 30$ K. As already mentioned, the $g_\parallel$-value deviates from g_e due to the contribution of the Co($3d_{x^2-y^2}$) orbital. Thus the observed increase of the $g_\parallel$-value is attributable to the increasing contribution of this orbital. This interpretation is seen to be reasonable if one considers the destabilization

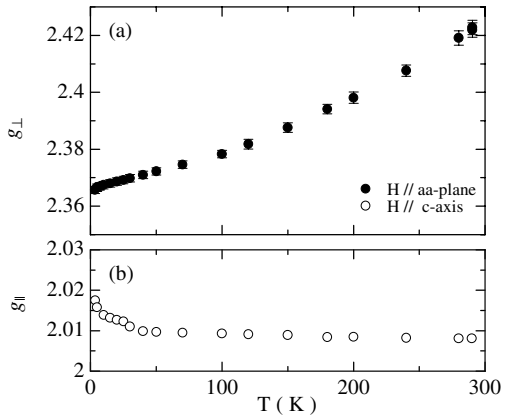

Figure 5. Temperature dependences of the principal g-values: (*a*) $g_\perp$ and (*b*) $g_\parallel$.

of the Co($3d_{z^2}$) orbital in the low-temperature region as discussed above, because it reduces the energy separation between the Co($3d_{x^2-y^2}$) and Co($3d_{z^2}$) orbitals, which may promote the mixing of these two orbitals.

As already mentioned, ΔH_{pp} also shows clear anisotropy in the ac-plane and this type of anisotropy is observed over the whole temperature region as shown in figure 6, where open and closed circles represent $\boldsymbol{H}$ parallel to the c-axis and within the aa-plane, respectively. As mentioned before, the temperature dependence of the spin susceptibility χ suggests that there is a finite antiferromagnetic superexchange interaction of $J \simeq 4.9$ K between Co^{II} ions, which is estimated from $\theta \simeq 4.9$ K for number of nearest-neighbour Co^{II} ions $Z = 2$ and $S = 1/2$. As a result, the eight hyperfine splitting lines of the ESR spectra due to ^{59}Co nuclei ($I = 7/2$) are averaged out into a single amalgamated line (exchange narrowing). In this case, it is natural to consider the exchange-narrowed hyperfine splitting as the origin of the observed ΔH_{pp}. Then ΔH_{pp} contains the remaining information on the anisotropy and amplitude of the original hyperfine interaction, although the estimation of the hyperfine splitting energy itself is difficult and there remains some ambiguity. For estimating the exchange-narrowed linewidth, Anderson and Weiss have presented the following expression [12]:

$$\Delta H = [(10/3)H_p^2 + H_H^2]/H_e, \tag{2}$$

where ΔH represents the half-width at half-power, H_p, H_H and H_e represent the internal magnetic field due to dipole, hyperfine and exchange interactions, respectively. The first term of equation (2) is negligible due both to the large separation between Co^{II} ions and to the relatively large value of H_e. In fact, the lattice parameter and observed H_e lead to a prediction of at most 0.04 G for the dipole interaction term of equation (2) at room temperature, which is three orders of magnitude smaller than the experimental value of ΔH_{pp}. Then on replacing H_H with $7|A|$, the largest splitting of the ESR line between $m_I = \pm 7/2$ transitions, equation (2) reduces to the following form:

$$\Delta H = 49A^2/H_e, \tag{3}$$

where $|A|$ represents the hyperfine splitting constant. In the low-spin d^7 electron configuration with the unpaired electron residing on the d_{z^2} orbital, crystal-field calculation provides the following relations for the principal $|A|$-values [9, 13, 14]:

$$A_\perp = -P[\kappa + 2/7 - (15/14)(\Delta g_\perp)] \tag{4}$$

$$A_\parallel = -P[\kappa - 4/7 + (1/7)(\Delta g_\perp)], \tag{5}$$

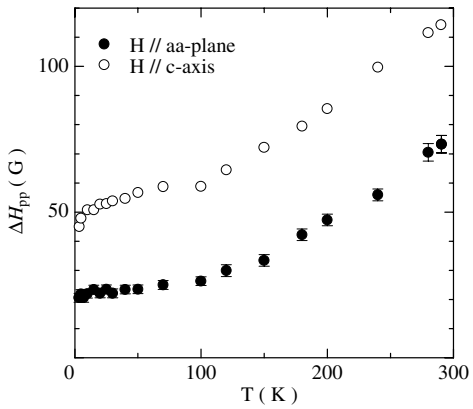

Figure 6. Temperature dependences of the ESR linewidth ΔH_{pp} with $\boldsymbol{H}$ parallel to the c-axis (open circles) and within the aa-plane (solid circles).

where κ is the isotropic Fermi contact term and $P = g_e g_N \beta_e \beta_N < 3\,d_{z^2}|r^{-3}|3d_{z^2} >$ (=0.022 cm^{-1} for free Co^{II} ions [15]). $\Delta g_\perp$ represents the shift of $g_\perp$-value from g_e which is given in equation (1). Using these equations, we discuss the observed behaviours of ΔH_{pp} in this material. As shown in figure 6, ΔH_{pp} along the c-axis is larger than ΔH_{pp} along the a-axis over the whole temperature region. As predicted from equation (5), this is attributable to the anisotropy of $|A|$, i.e., $|A_\parallel| > |A_\perp|$. This type of anisotropy is often seen in the low-spin Co^{II} complexes [14, 16, 17]. In addition, figure 2 further suggests that the g- and A-tensors of this material have the same principal axes because the extremal values of g and ΔH_{pp} are observed at the same angles within experimental error. We mention here the order estimation for the $|A|$-values, fixing H_e to the experimentally obtained J of 4.9 K ($\simeq$30 000 G). At $T = 70$ K, equation (3) predicts $|A_\perp| \simeq 125$ G and $|A_\parallel| \simeq 190$ G. These values are comparable to the typical value of 170 G, which is given by Yudanova *et al* for the analogous complexes Co(tpp)·$C_{60}(CS_2)_{0.5}$ and Co(tpp)·C_{70} [18, 19].

On the other hand, ΔH_{pp} shows remarkable broadening along both axes especially in the high-temperature region as shown in figure 6. There are two possibilities for explaining this temperature dependence of ΔH_{pp}, i.e., the temperature variation of the $|A|$-values due to the shift of the $g_\perp$-value and the dominance of the spin–lattice relaxation time T_1 at higher temperatures. The former possibility is, however, excluded by the following consideration. Since the third terms of equation (5) for both principal axes are proportional to the temperature-dependent value of $\Delta g_\perp$ which is shown in figure 5(a), the $|A|$-values can be modified as the temperature increases. But in such a case, equation (5) allows the $|A|$-value to increase with temperature only for one principal axis and not for both axes. For example, if we adopt the experimentally obtained $\Delta g_\perp$ values for this material and $\kappa \simeq 0$, which is observed for the Co^{II} phthalocyanine complex [13], equation (5) shows that $|A_\perp|$ will increase with the $\Delta g_\perp$ value, but $|A_\parallel|$ will, in contrast, decrease as the temperature increases. Furthermore, no matter how the value of κ is adjusted, equation (5) is incapable of explaining the observed behaviour of ΔH_{pp}. Thus it is concluded that the smaller value of T_1 at higher temperatures should be the main origin of the observed broadening of ΔH_{pp}. It is reported that the square-planar Co^{II}(tpp) complex exhibits no ESR spectra at room temperature due to a small T_1-value [19, 20]. This may be consistent with the observation of line broadening for the current material. It should be noted that the dominance of the spin–lattice relaxation time in the high-temperature region would not change the estimation of $|A|$-values at 70 K discussed above because it is expected that T_1 will becomes larger rapidly with decreasing temperature [21].

On the basis of the ESR measurements above, the electronic ground state of Co(tbp)·C_{60} has become clear and the features of the temperature-dependent intermolecular interaction between Co(tbp) and C_{60} are clarified. As the next step, photoinduced changes of ESR spectra may provide information on the charge transfer from Co(tbp) to fullerene. Such measurements are now under way.

4. Conclusions

We made ESR measurements on the newly synthesized cocrystallite of C_{60} with the Co^{II}(tbp) complex. Both the spin susceptibility χ and the absence of ^{59}Co hyperfine structure suggest the existence of a superexchange interaction between Co^{II} ions via the C_{60} molecule in this material. We found temperature-dependent g-values, this dependence arising from the increase in crystal-field splitting energy of the Co(3d) orbitals, providing evidence of the increase in intermolecular interaction as the temperature is lowered. This result is consistent with the x-ray structural analyses which show that the intermolecular distance between Co^{II}(tbp) and C_{60} decreases with temperature. In addition, temperature-dependent ESR linewidths are observed along both axis, which may be attributable to the shorter spin–lattice relaxation time in the high-temperature region.

Acknowledgment

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References

[1] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162
[2] Hebard A F, Rosseinski M J, Haddon R C, Murphy D W, Glarum S H, Palstra T T M, Ramirez A P and Kortan A R 1991 *Nature* **350** 600
[3] Allemand P M, Khemani K C, Koch A, Wudl F, Holczer K, Donovan S, Gruner G and Thompson J D 1991 *Science* **253** 301
[4] Olmstead M M, Costa D A, Maitra K, Noll B C, Phillips S L, Van Calcar P M and Balch A L 1999 *J. Am. Chem. Soc.* **121** 7090
[5] Hochmuth D H, Michel S L J, White A J P, Williams D J, Ballet A G M and Hoffman B M 2000 *Eur. J. Inorg. Chem.* 593
[6] Ishii T, Aizawa N, Yamashita M, Matsuzaka H, Kodama T, Kikuchi K, Ikemoto I and Iwasa Y 2000 *J. Chem. Soc. Dalton Trans.* **23** 4407
[7] Ishii T, Aizawa N, Kanehama R, Yamashita M, Matsuzaka H, Kodama T, Kikuchi K and Ikemoto I 2001 *Inorg. Chim. Acta* **317** 81
[8] Ishii T, Kanehama R, Aizawa N, Yamashita M, Matsuzaka H, Sugiura K, Miyasaka H, Kodama T, Kikuchi K, Ikemoto I, Tanaka H, Marumoto K and Kuroda S 2001 *J. Chem. Soc. Dalton Trans.* 2975
[9] Maki A H, Edelstein N, Davison A and Holm R H 1964 *J. Am. Chem. Soc.* **86** 4580
[10] Nowlin T, Subramanian S and Cohn K 1972 *Inorg. Chem.* **11** 2907
[11] Allemand P-M, Srdanov G, Koch A, Khemani K and Wudl F 1991 *J. Am. Chem. Soc.* **113** 2781
[12] Anderson P W and Weiss P R 1953 *Rev. Mod. Phys.* **25** 269
[13] Griffith J S 1958 *Discuss. Faraday Soc.* **26** 81
[14] Wayland B B, Minkiewicz J V and Abd-Elmageed M E 1974 *J. Am. Chem. Soc.* **96** 2795
[15] Abragam A and Pryce M H L 1951 *Proc. R. Soc.* **206** 173
[16] Walker F A 1970 *J. Am. Chem. Soc.* **92** 4235
[17] Symons M C R and Wilkinson J G 1971 *J. Chem. Soc.* A 2069
[18] Konarev D V, Yudanova E I, Neretin I S, Slovokhotov Yu L and Lyubovskaya R N 2001 *Synth. Met.* **121** 1125
[19] Yudanova E I, Konarev D V, Gumanov L L and Lyubovskaya R N 1999 *Russ. Chem. Bull.* **48** 718
[20] Assour J M 1965 *J. Chem. Phys.* **43** 2477
[21] Orton J W 1968 *Electron Paramagnetic Resonance* (London: Iliffe) ch 9