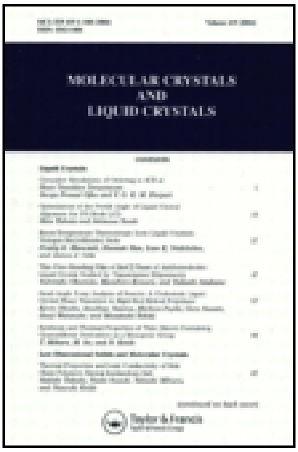

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g -Tensor Analyses of β′-Type Pd(dmit) 2 Metal Complexes

Toshikazu Nakamura [a], Toshihiro Takahashi [b], Shuji Aonuma [c] & Reizo Kato [d]

[a] Institute for Molecular Science, Okazaki, 444-8585, Japan

[b] Department of Physics, Gakushuin University, Mejiro 1-5-1, Toshimaku, Tokyo, 171-8588, Japan

[c] Department of Materials Science, Osaka Electro-Communication University, 18-8 Hatsu-Cho, Neyagawa, Osaka, 572-8530, Japan

[d] The Institute of Physics and Chemical Research, 2-1 Hirosawa, Wako-shi, Saitama, 351-0198, Japan

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g-Tensor Analyses of β′-Type $Pd(dmit)_2$ Metal Complexes

TOSHIKAZU NAKAMURA[a], TOSHIHIRO TAKAHASHI[b],
SHUJI AONUMA[c] and REIZO KATO[d]

[a]*Institute for Molecular Science, Okazaki 444-8585, Japan,*
[b]*Department of Physics, Gakushuin University, Mejiro 1-5-1, Toshimaku, Tokyo 171-8588, Japan,*
[c]*Department of Materials Science, Osaka Electro-Communication University, 18-8 Hatsu-Cho, Neyagawa, Osaka 572-8530, Japan and*
[d]*The Institute of Physics and Chemical Research, 2-1 Hirosawa, Wako-shi, Saitama, 351-0198, Japan*

ESR measurements and g-tensor analyses were performed for metal complexes, β'-type $Pd(dmit)_2$. The ESR g-values of β'-type $Pd(dmit)_2$ are found to be beyond one radical description which is a good approximation for conventional molecular based conductors. In this paper we focus on the anomalous behavior of the ESR g-values in β'-type $Pd(dmit)_2$. We discuss the possible explanation of the electronic structure of β'-type $Pd(dmit)_2$ metal complexes from microscopic points of view.

Keyword metal complexes; dmit; ESR

INTRODUCTION

Metal dithiolene complexes, $Pd(dmit)_2$ (where the dmit is the 1,3-dithia-2-thione-4,5-dithiolato), are one of the major families in organic conductors. While $R_4Z[Pd(dmit)_2]_2$ compounds show metallic behavior at room temperature, the low temperature phases are paramagnetic insulators.[1,2] In order to clarify the mechanism of the charge localization of β'-type Pd(dmit)$_2$ compounds, we carried out magnetic resonance measurements.[3–7] Although they are isostrcural and with little differences in lattice parameters, the ESR parameters show different behavior with counter cations. As mentioned in the previous report,[7] we found a close relation between the antiferromagnetic transition temperature, T_{N} and inter-stack interaction. However, several problems remain unsolved. In this paper, we focus on the anomalous behavior of the ESR g-values in β'-type Pd(dmit)$_2$. We discuss the electronic structure of β'-type Pd(dmit)$_2$ metal complexes from microscopic points of view.

EXPERIMENTAL

Sample preparation and crystal structural data were shown in previous reports.[2,8–10] The ESR measurements were carried out for $1 \sim 10$ aligned single crystal(s) using an X-band spectrometer JES-FE3XG (JEOL) equipped with an Air Products continuous-flow cryostat LTR-3 (between 100 K and 7 K) ; experimental details were shown in ref. 11. In order to investigate lower temperatures, the Et$_2$Me$_2$Sb was also measured using an X-band spectrometer ESP-300E (Bruker) equipped with an Oxford continuous-flow cryostat down to 4 K. We confirmed the consistent of the results measured by both equipments.

RESULTS AND DISCUSSION

The ESR measurements were performed for β'-R_4Z[Pd(dmit)$_2$]$_2$ with counter cations of Me$_4Z$ (Z= As and Sb) and Et$_2$Me$_2Z$ (Z= P, As and Sb). Hereafter, we classify the experimental results into following three groups; (a) compounds with T_{N} around 35 K, (b) compounds with T_{N} around 18 K, and (c) compounds with T_{N} below experimental limitation (4 K). Since no significant difference was found among

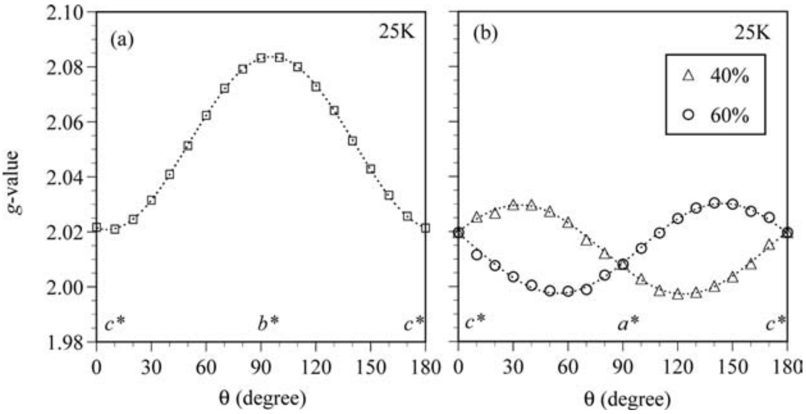

FIGURE 1 Angular dependence of the g-values of of Et$_2$Me$_2$P salts at 25 K.

the compounds in the same group, we show the experimental results for the typical compounds of each groups; the results of (a) Me$_4$As, (b)Et$_2$Me$_2$P and (c)Et$_2$Me$_2$Sb cations are shown. Scattering of data at high temperatures is due to weak ESR signals associated with huge broadening of the linewidth.

The anisotropy of the g-values is huge even in the case of the external field applying in the conduction plane. These features are different from TTF based organic conductors where the in-plane anisotropy of the g-values is small and the g-value shows a maximum when the external field applied perpendicular to the conducting plane.[11] Angular dependence of the g-values of Et$_2$Me$_2$P at 25 K was shown in Fig. 1. While the resonance signal is single in the a^*b^* plane rotation, it splits into two within the c^*a^* plane. The ratio of the relative intensity is approximately 6:4. Since the crystal structure is monoclinic and we used 10 aligned crystals for this measurement, two arrangements are possible when we put the a^*b^* plane of the crystals parallel to the ESR sample stage. Considering

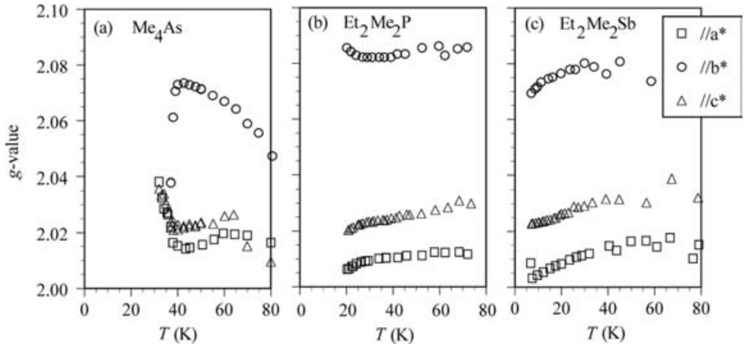

FIGURE 2 Temperature dependence of the g-values of β'-type $\mathrm{Pd(dmit)_2}$ compounds; (a) $\mathrm{Me_4As}$, (b) $\mathrm{Et_2Me_2P}$ and (c) $\mathrm{Et_2Me_2Sb}$ cations ($H_0\|a^*$(square), $\|b^*$(circle), $\|c^*$(triangle)).

this situation, we can evaluate the principal values and axes of the g-tensor by least squares fit to the measured data assuming anisotropic g-value.

The principal *axes* are well explained as the average of the molecular axes of $\mathrm{Pd(dmit)_2}$ radicals with solid crossing columns. On the other hand, the principal *values* of $\mathrm{Pd(dmit)_2}$ show characteristic features. The large shifts from g_e of the g_1 and g_2 are remarkable, while the small shift of the g_3 is explained by the fact that HOMO and/or LUMO are mainly composed of orbital elongating the z direction. Considering the huge shift of the g_1, it seems likely that the Pd $d_{3z^2-r^2}$ orbital also composes of the wave function besides the p_z orbital of C and S. It is noted that the principal value shows maximum for approximately molecular short axis, while the maximum principal values of TTF derivatives are along the molecular long axes. This fact suggests that there is small contribution of the Pd d orbital along the molecular long axis. However, an isolated

Pd(dmit)$_2$ possesses a HOMO without the d contribution because of its symmetry according to the extended Hückel Molecular orbital calculation. Moreover, the average of the principal values, $< g_{\mathrm{AV}} >$ (= 2.038), of β'-Et$_2$Me$_2$P salt does not agree with that of a 1:1 radical, Bu$_4$N[Pd(dmit)$_2$] (Bu=butyl) solution, $< g >$ (= 2.0191). The observed g-tensor cannot be explained by that of the isolated Pd(dmit)$_2$ molecule. It is likely that the discrepancy of the g-tensor from the isolated radical is due to the deformation of the wave-function with the strong dimer structure of the Pd(dmit)$_2$ system. Recent first-principle calculations by Miyazaki *et al.* including the actual dimer effect suggest that the HOMO of Pd(dmit)$_2$ has appreciable contributions from the Pd $d_{3z^2-r^2}$ orbitals. This expectation is coincided with the ESR results.

Figure 2 shows the temperature dependence of the g-values of typical compounds of three groups; (a) Me$_4$As, (b)Et$_2$Me$_2$P and (c)Et$_2$Me$_2$Sb cations, applying the external static field along the crystal axes. The g-values for all the directions are changing their absolute values with temperature. The change is pronounced in the b*-axis; approximately parallel to the molecular short axis. Especially, Me$_4$As salt shows crucial temperature dependence. Since the system possesses one kind of spin species, we cannot explain the anomalous behavior of the g-value by the orientation of the molecules. One of possible explanations is antiferromagnetic fluctuation. Significant g-shifts are observed in one-dimensional AF magnets just above T_{N}'s. However, in the case of Pd(dmit)$_2$, the onset temperatures of the g-shift seem to be too high considering the T_{N}. Antiferromagnetic fluctuation seems unlikely. Another possible explanation is a dimerization effect. As discussed above, the discrepancy of the principal values from those of the isolated radical is considered to be due to the strong dimer structure of the Pd(dmit)$_2$ system. Hence it seems likely that possible change of the magnitude of the dimerization causes the curious temperature dependence of the g-values. Further investigations are now going on.

In conclusion, we measured the g-values and performed the g-tensor analyses for the family of Pd(dmit)$_2$ metal complexes. The ESR g-values of Pd(dmit)$_2$ are found to be beyond one radical description; we should consider the wave-function [Pd(dmit)$_2$]$_2$ supramolecules.

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