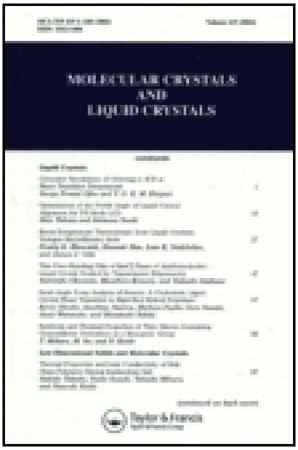

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Low Temperature Electronic States of β'-Type $Pd(dmit)_2$ Compounds

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Magnetic resonance investigations of metal dithiolene complexes, β'-$R_4Z[Pd(dmit)_2]_2$, have been performed. Although they are isostructural with little differences in lattice parameters, their spin-spin correlation and antiferromagnetic transition temperature, T_N, show huge sample dependence. We found a close relationship between the T_N and inter-dimer interactions. The low temperature electronic states of a series of molecular conductors based on $Pd(dmit)_2$ at ambient pressure are discussed from microscopic points of view.

Keywords: dmit; EPR; antiferromagnetic transition

INTRODUCTION

Research of metal dithiolene complexes, $M(dmit)_2$ (where the dmit is the 1,3-dithia-2-thione-4,5-dithiolato), is one of major trend in the development of organic conductors with new functions. Although several metallic compounds even at ambient pressure are observed in $Ni(dmit)_2$ compounds[1], most of $Pd(dmit)_2$ compounds (especially β(')-type one) show paramagnetic non-metallic behavior at ambient pressure.[2,3] Since the crystal structure of the Pd(dmit)$_2$ system is based on stacks of strongly dimerized Pd(dmit)$_2$ molecules, the energy levels of the antibonding HOMO band possibly become higher than that of bonding LUMO.[4] As a result, the conduction band is considered to be formed by the two-dimensional half-filled HOMO band. Hence the non-metallic state of β(')-type Pd(dmit)$_2$ compounds at ambient pressure is believed to be a Mott-Hubbard insulator. In facts, we found clear antiferromagnetic transitions in Pd(dmit)$_2$ and its selenium-containing analog, Pd(dmise)$_2$ compounds by ^{1}H-NMR measurements[5,6], which ruled out the possibility of an SDW transition. However, several problems remain unsolved; for example, the local magnetizations and T_N are different between the Pd(dmit)$_2$ and the Pd(dmise)$_2$ based compounds. The main aim of this study is to determine the antiferromagnetic state and to clarify the electronic states by systematic investigations of Pd(dmit)$_2$ salts. We performed the EPR measurements for an isostructural series of β'-Et$_2$Me$_2$$Z$ and Me$_4$$Z$[Pd(dmit)$_2$]$_2$ (Me=methyl; Et=ethyl). We discuss the electronic states of the Pd(dmit)$_2$ compounds in the aspect of strong dimer system.

EXPERIMENTAL

Sample preparation and crystal structural data were shown in previous reports.[3,7–9] The EPR measurements were carried out for 1 ~ 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. [10]. 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

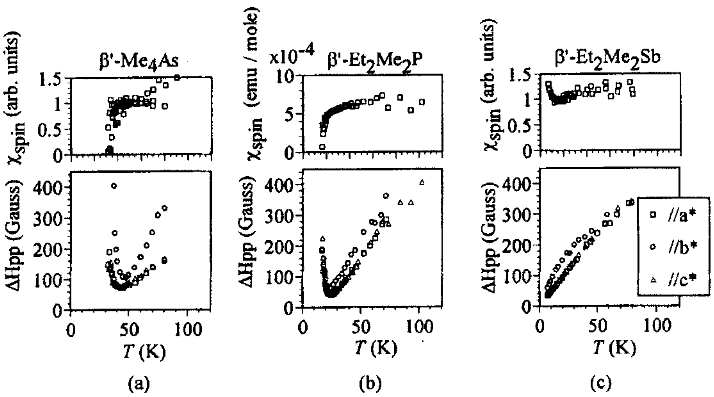

FIGURE 1 Temperature dependence of the χ_{spin} determined by EPR intensity and ΔHpp of β'-type Pd(dmit)$_2$ compounds; (a) Me$_4$As, (b) Et$_2$Me$_2$P and (c) Et$_2$Me$_2$Sb cations ($H_0 \| a^*$(square), $\| b^*$(circle), $\| c^*$(triangle)).

confirmed the consistent of the results measured by both equipments.

RESULTS AND DISCUSSION

We have performed ESR measurements for Pd(dmit)$_2$ compounds with counter cations of Me$_4Z$ ($Z=$ As and Sb) and Et$_2$Me$_2Z$ ($Z=$ P, As and Sb). The experimental results can be roughly classified 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). Figure 1 shows the temperature dependence of the χ_{spin} determined by Electron Paramagnetic Resonance (EPR) intensity and ΔHpp of typical compounds of three groups; (a) Me$_4$As, (b)Et$_2$Me$_2$P and (c)Et$_2$Me$_2$Sb cations. Scattering of data at high temperatures are due to weak EPR signals associated

Cation	Et_2Me_2Sb	Et_2Me_2As	Et_2Me_2P	Me_4Sb	Me_4As	Me_4P
T_N	< 4	18	18	18	35	35

TABLE 1 Determined T_N of the β(')-type $Pd(dmit)_2$ compounds

with huge broadening of the linewidth. Sudden disappearance of the EPR signal (below 35 K in (a) and below 18 K in (b)) suggests a phase transition. At the same temperatures, divergence of the ΔH_{pp} was observed, indicating magnetic long-range order. The determined T_Ns are summarized in Table 1.

One of the questions that arise from above results is "Why does the T_N of $Pd(dmit)_2$ show crucial sample dependence?" Recently Rouziére *et al.* discussed variations in the electronic structures in relation with the structural changes and with the influence of the cation on the crystal from the point of view of X-ray diffraction investigation.[9] They estimated 'inter'-dimer overlap integrals, since the strong dimerization of the $Pd(dmit)_2$ enhances the two-dimensional character of HOMO through HOMO-LUMO level-crossing. If we adopt the parameters in ref. [9], the normalized 'inter'-dimer interaction within stacks, B/A, and that between stacks, r/A, we found a close relationship between the T_N and these parameters as shown in Fig. 2. The T_N seems to decrease as the B/A decreases, and the r/A increases. It is noted that the T_N decreases as the r/B approached to 1 from 0.5. It is noted that magnetic order has not been observed down to 4 K in the Et_2Me_2Sb cation salt where the $r/B \sim 1$. Recently a theoretical investigation of effective exchange interactions for dimerized systems was performed by Mori *et al.*[11] They show two possible ground states depending on the symmetry of the wave-function. Assuming that the HOMO levels are dominant

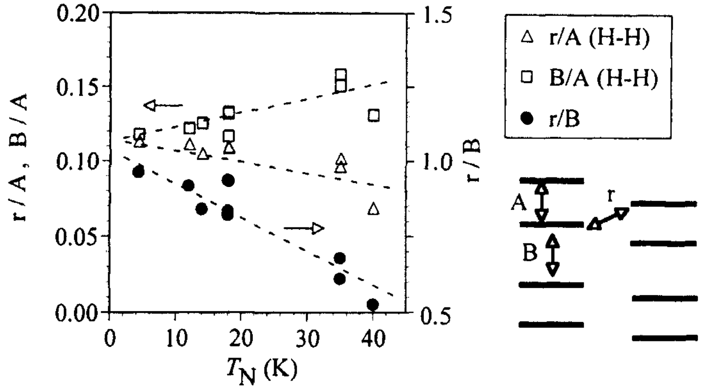

FIGURE 2 Relationship between the inter-dimer interaction versus the T_N. Previous results determined by ^{1}H-NMR are also included in this figure. The parameters, A, B and r, which are shown in the schematically shown in insets, are same in ref. [9]. The Broken line is a guide to the eye.

for magnetic interactions, the T_N and magnitude of local moments are reduced by the competition between J_1 (intra-stack interaction) and J_2 (inter-stack interaction). The calculated T_N and magnitude of local moments for Pd(dmit)$_2$, are in agreement with the EPR and ^{1}H-NMR results.

Huge anisotropy of the g-values is one of the characteristic features of Pd(dmit)$_2$ compounds. One of the principal axes, g_1 (=2.0085), lies along the b-axis, which is roughly direction along the molecular short axis. The g_2 (=2.030) lies along the molecular long axis, and g_3 (=2.000) is close to the direction normal to the molecular plane. The direction of the principal axes are well explained as the average of the molecular axes of Pd(dmit)$_2$ radicals with solid crossing columns. However the principal values (and the symmetry of the wave-function !) are found to be beyond one radical description; we should consider the wave-function $[Pd(dmit)_2]_2$ supermolecules.

In conclusion, we investigated the low temperature electronic state of β'-type $Pd(dmit)_2$ compounds. We found a close relationship between the T_N and the inter-dimer interaction. It seems likely that possible competition between the intra-stack and inter-stack dimer-dimer interactions reduces the T_Ns and magnitude of the local moments. NMR investigations for ^{13}C substituted $Pd(dmit)_2$ molecules are in progress. Preliminary results of ^{13}C-NMR spin-lattice relaxation rate, ^{13}C-$T_1{}^{-1}$, shows a considerable antiferromagnetic fluctuation in paramagnetic states. Divergence of the ^{13}C-$T_1{}^{-1}$ just above the T_N indicates a three-dimensional magnetic long-range order. Detailed analysis of the NMR results will be discussed elsewhere.

Acknowledgments

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