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High Pressure X-ray Crystal Structure Analysis of $Pd(dmit)_2$ Salts

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We have performed X-ray diffraction study under pressure for isostructural anion radical salts β'-$Et_2Me_2Z[Pd(dmit)_2]_2$ (Z = P, As, Sb) at room temperature. The unit cells remained monoclinic and no satellite reflection was detected up to 18 kbar. For the high-pressure superconductor Et_2Me_2P salt, high-pressure crystal structure analyses were carried out. Obtained band parameters indicate an increase of bandwidth and a decrease of the dimensionality of a HOMO-based band. This is related to a pressure-induced metallic state and a non-metallic state in the higher pressure region.

Keywords: molecular conductor; metal dithiolene complex; crystal structure; pressure effect

INTRODUCTION

Crystal structure of β'-$Pd(dmit)_2$ anion radical salts is characterized by a solid-crossing columns composed by strongly dimerized $Pd(dmit)_2$ units (Figure 1). This is a unique two-band system associated with two-dimensional HOMO-based band and one-dimensional LUMO-based band[1,2]. The inversion of the energy levels is induced by the strong dimerization, and the HOMO-based band becomes a

half-filled conduction band. These salts are considered Mott-like insulators at ambient pressure. Several compounds show metallic and superconducting states under pressure which are followed by a non-metallic state under higher pressure region[3,4]. Such a behavior is thought to be due to an overlap of these two bands and a reduction in the dimerization under pressure[1].

We carried out X-ray diffraction study for β'-$Et_2Me_2Z[Pd(dmit)_2]_2$ (Z = P, As, Sb) under pressure at room temperature (RT) to clarify the nature of the electronic states. The high-pressure crystal structure analyses for the high-pressure superconductor Et_2Me_2P salt (T_c = 4 K at 7 kbar)[4] were performed.

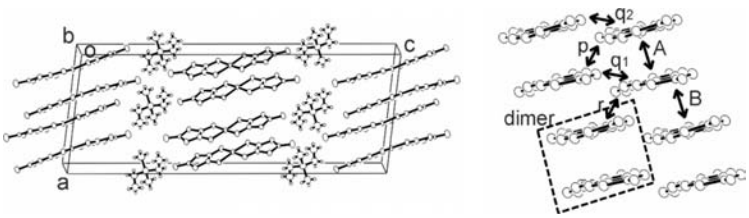

FIGURE 1 Crystal structure of β'-$Et_2Me_2P[Pd(dmit)_2]_2$.

EXPERIMENTAL

We measured the X-ray diffraction of the single crystals under pressure using a diamond anvil cell. The value of pressure was determined by the powder pattern of NaCl. The pressure medium is methanol-ethanol (4:1) mixture. X-ray diffraction data under pressure were collected by imaging plate type Weissenberg camera (Mac Science DIP320V) with graphite-monocromated Mo *K*α radiation. The structure was refined by

the rigid body model. Anisotropic thermal parameters for Pd and S atoms, and isotropic thermal parameters for C and P atoms were applied. Crystal data are given in Table 1.

TABLE 1 Crystal data for β '-$Et_2Me_2P[Pd(dmit)_2]_2$ at RT.

	1bar	7.0kbar	13.6kbar
space group	C2/c	C2/c	C2/c
a/Å	14.356(1)	14.160(1)	14.032(1)
b/Å	6.3390(4)	6.1980(5)	6.1500(5)
c/Å	37.646(2)	37.241(3)	37.086(3)
β/deg	95.832(5)	96.988(6)	97.315(7)
V/Å^3	3408.2(4)	3244.1(4)	3174.4(5)
no. of observed ref.(I>2σ(I))	1024	862	900
R	0.103	0.107	0.138

RESULT AND DISCUSSION

Figure 2 shows lattice parameters for β '-$Et_2Me_2Z[Pd(dmit)_2]_2$ (Z=P, As, Sb) at RT as a function of pressure which are normalized by the ambient-pressure values. In every salt, the monoclinic symmetry was retained and no satellite reflection was observed within the measured pressure range. These parameters exhibited similar trends; the values along the *a*, *b* and *c*-axes decrease monotonously, while the *β* value increases. Such a behavior in the constriction corresponds to that in the thermal contraction at ambient pressure[5].

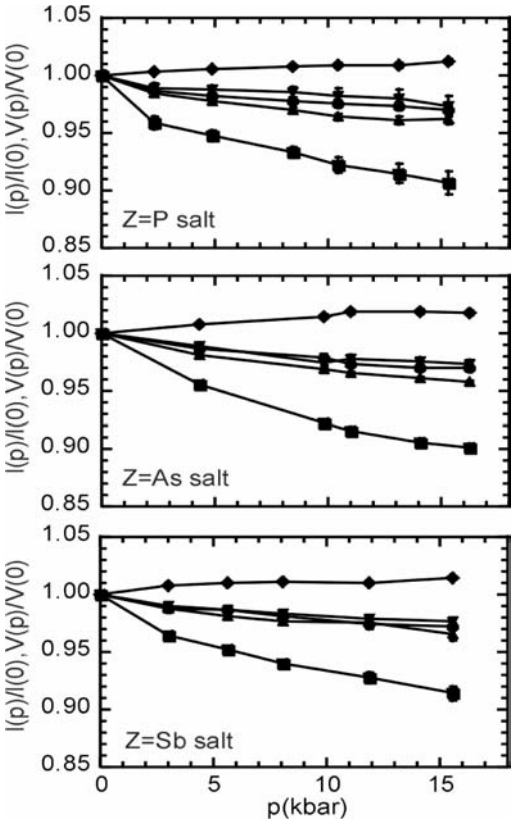

FIGURE 2 Normalized lattice parameters as a function of pressure for β'-$Et_2Me_2Z[Pd(dmit)_2]_2$ (Z=P, As, Sb). Symbols are defined as *a* (●), *b*(▲), *c*(▼), β(♦) and *V*(■).

Crystal structure analyses under high pressure were performed for the Et_2Me_2P salt. Inter-planar distances between $Pd(dmit)_2$ units are given in Table 2. We note that the degree of diminution of the inter-dimer distance (d_{inter}) is larger than that of the intra-dimer distance (d_{intra}).

The intermolecular overlap integrals among HOMO and LUMO calculated with the extended Hückel method are shown in Table 3. These values indicate that the dimerization gap[1] is slightly enhanced with applying the pressure, and the width of the conduction band is broadened up to 7 kbar and then saturated in the higher pressure region. Consequently, as an origin of the high-pressure metallic state in the Et_2Me_2P salt, the increase of the bandwidth is more plausible than the band overlap. The dimensionality of the HOMO-based band defined by the ratio r/B decreases significantly under higher pressure, which introduces a one-dimensional character of the band. In the previous

TABLE 2 Inter-planar distances in β'-$Et_2Me_2P[Pd(dmit)_2]_2$.

	1bar	7.0kbar	13.6kbar	8K(1bar)[5]
d_{intra} (Å)	3.269	3.248	3.232	3.249
d_{inter} (Å)	3.765	3.629	3.559	3.675

TABLE 3 Overlap integrals S($\times 10^3$) (defined in Figure 1) among HOMO and LUMO for β '-$Et_2Me_2P[Pd(dmit)_2]_2$.

	1bar			7.0kbar			13.6kbar		
	L-L	H-H	H-L	L-L	H-H	H-L	L-L	H-H	H-L
A	44.82	-45.45	-0.89	46.95	-49.70	-4.11	49.18	-49.99	-2.83
B	-3.42	-5.11	-1.24	-4.81	-8.11	-2.71	-5.85	-7.94	-3.57
p	1.41	-2.31	-0.77	1.95	-3.22	-1.33	2.15	-3.28	-1.43
q1	-1.01	-1.75	0.19	-1.39	-2.41	0.28	-1.43	-2.26	0.32
q2	-1.01	-1.75	0.73	-1.38	-2.39	0.85	-1.47	-2.98	0.70
r	2.11	-5.17	-1.40	2.50	-5.74	-1.74	2.66	-4.49	-1.36
r/B	0.62	1.01		0.52	0.71		0.46	0.57	

paper, the high-pressure (>11 kbar) non-metallic state was understood by the one-dimensional instability affected by the LUMO-based band. The results obtained in this work, however, suggest that this non-metallic state comes from the increase of one-dimensional character of the HOMO-based band.

In summary, we have performed X-ray diffraction measurement under pressure for β'-$Et_2Me_2Z[Pd(dmit)_2]_2$ (Z = P, As, Sb). From the high-pressure structure analyses, we found the increase of the bandwidth and the enhancement of one-dimensional character for the HOMO-based band under pressure. This is relevant to the appearance of the metallic state and higher-pressure non-metallic state in the Et_2Me_2P salt.

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