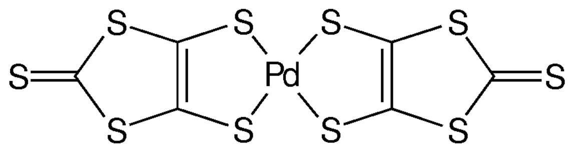
A New Series of Conducting Anion Radical Salts, $EtMe_3Z[Pd(dmit)_2]_2$ (Z=N, P, As, Sb) –Various Mott-insulating States and their Release under Pressure–

Reizo Kato,[1,2] Akiko Nakao,[1,2] Akiko Tajima,[1] Atsuko Fukaya,[1] Jun-ya Eda,[3] Masafumi Tamura[1,2]
[1]RIKEN, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan
[2]JST-CREST, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan
[3]Department of Physics, Toho University, Funabashi, Chiba 274-8510, Japan
E-mail; reizo@riken.jp

Five conducting $EtMe_3Z$ (Z=N, P, As, Sb) salts of the metal dithiolene complex $Pd(dmit)_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) have been prepared by the air-oxidation of the corresponding 2:1 salts. Their crystal data at room temperature are listed in Table 1. There are three structural types with the space groups, *P21/m*, *P1*, and *C2/c*, all of which are based on a strongly dimerized $Pd(dmit)_2$ unit. The $[Pd(dmit)_2]_2^-$ dimers form a two-dimensional quasi triangular lattice.

They belong to the strongly correlated system. At ambient pressure, all of them are Mott insulators where one electron is located on each dimer. The localized electrons exhibit various magnetic behaviors. The $EtMe_3Sb$ salt, where the deviation from the regular triangular lattice is small, shows frustrated paramagnetism down to the lowest temperature. The $EtMe_3As$ salt with larger deviation from the regular triangular lattice undergoes an antiferromagnetic transition at 23 K. The $EtMe_3P$ salt ($P2_1/m$) shows a spin-Peierls-like phase transition to a non-magnetic state at 25 K, which is the first case in a two-dimensional spin system close to the triangular lattice. The $EtMe_3N$ salt shows a second-order phase transition to a non-magnetic state at 85 K and the $EtMe_3P$ (*P1*) salt also shows a second-order phase transition at 73 K. Mechanisms for these second-order transitions consistent with low-temperature crystal structures have not been found out.

The application of hydrostatic pressure can release the Mott-insulating state and induce a metallic or superconducting state. The $EtMe_3P$ ($P2_1/m$) and $EtMe_3As$ salts exhibit the superconductivity at 5 K (3.3 kbar) and at 4 K (7 kbar), respectively. It is quite interesting that **these two superconducting states would be associated with different types of Mott-insulating states: the spin Peierls-like non-magnetic state and the antiferromagnetic state**.



Pd(dmit)$_2$

Table 1 Crystal Data of $EtMe_3Z[Pd(dmit)_2]_2$ at room temperature.

Cation	$EtMe_3N$	$EtMe_3P$	$EtMe_3P$	$EtMe_3As$	$EtMe_3Sb$
Space group	$P2_1/m$	$P2_1/m$	*P1*	*C2/c*	*C2/c*
a / Å	6.2650(4)	6.3960(3)	7.7810(5)	14.4690(6)	14.5220(5)
b / Å	36.520(2)	36.691(1)	18.621(1)	6.3790(3)	6.4080(2)
c / Å	7.7340(5)	7.9290(3)	6.3220(4)	37.328(2)	37.302(1)
α / °	—	—	97.246(5)	—	—
β / °	108.932(4)	114.302(2)	109.761(4)	96.987(4)	97.365(3)
γ / °	—	—	84.194(4)	—	—
V / Å^3	1673.8(2)	1695.9(1)	853.5(1)	3419.7(3)	3442.6(2)
Z	2	2	1	4	4