STRUCTURES AND PHYSICAL PROPERTIES OF PLATINUM-DMIT RADICAL ANION SALTS

M. Nomura,¹ A. Tajima,¹ H.-B. Cui,¹ M. Abdel Jawad,¹ T. Tsumuraya,¹,² Y. Oshima,¹ T. Miyazaki,² R. Kato¹

¹Condensed Molecular Materials Laboratory, RIKEN, 2-1, Hirosawa, Wako-shi, Saitama 351-0198, Japan
mitsushiro@riken.jp (M.N.), reizo@riken.jp (R.K.)

²National Institute for Materials Science (NIMS), 1-1-1, Ten-noudai, Tsukuba, Ibaraki 305-8573, Japan

Most anion radical salts of the Pd-dithiolene complex \([\text{Pd}(\text{dmit})_2]\) (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) are Mott-insulators at ambient pressure. The \([\text{Pd}(\text{dmit})_2]_2\) dimer units form a triangular lattice in the crystal and then provide interplay between electron correlation and spin frustration.[1] We can precisely tune the electronic properties by applying physical stimuli to the crystal or chemical modifications (chemical pressure) of the salt. In the \([\text{Pd}(\text{dmit})_2]_2\) salts with quaternary onium cations, the so-called \(\beta\)- or \(\beta'\)-(R₄Z)[Pd(dmit)₂]₂ (R = Me and Et; Z = N, P, As and Sb), a chemical modification of the R₄Z⁺ cation systematically controls degree of the inter-dimer transfer integrals and thus anisotropy of the triangular lattice. On the other hand, we may control the intra-dimer transfer integral by Pd/Pt substitution, because an intra-dimer M–M distance is probably modified. However, the \(\beta\)- or \(\beta'\)-(R₄Z)[Pt(dmit)₂]₂ salt was rarely reported. To our knowledge, only the example in this series has been the \(\beta\)-(Me₄N)[Pt(dmit)₂]₂.[²]

Accordingly, we have decided to study the structures and physical properties of other (RMe₃Z)[Pt(dmit)₂]₂ salt (R = Me and FCH₂; Z = N, P, As and Sb) as shown in Fig. 1.

The ammonium cation salts (RMe₃N)[Pt(dmit)₂]₂ (RMe₃N⁺ = Me₄N⁺ and (FCH₂)Me₃N⁺) were obtained as the \(\beta\)-forms, whereas the other salts belonged to the \(\beta\)-form (RMe₃Z⁺ = Me₄P⁺, Me₄As⁺ and Me₄Sb⁺). The [Pt(dmit)₂] molecules were dimerized more weakly than those of [Pd(dmit)₂]. In contrast to the Mott-insulating [Pd(dmit)₂]₂ salts, the \(\beta\)-(FCH₂)Me₃N⁺ and the other \(\beta\)-Me₄Z⁺ salts of [Pt(dmit)₂]₂ showed metallic behavior under ambient pressure in the high temperature region. We consider that the introduction of Pt atom reduces on-site Coulomb energy and then induces metallic behavior. Furthermore, a metal-to-insulator transition appeared in the temperature range of 150-215 K, suggesting existence of charge-ordered states below the critical temperature. The band structures of these salts obtained by first-principles calculations will be also discussed.