

Hybridized Molecular Materials Based on $[\text{Mn}^{\text{III}}_2]$ Single Molecule Magnets with Molecular Conductors Formed by Metal Dithiolene Complexes

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Hybridized complexes have aroused a great deal of interests as multifunctional materials exhibiting more than two types of physical properties such as ferromagnetism and electrical conductivity [1]. The authors have opened door to the design of ferromagnetism/highly conductive hybrid materials based on $[\text{Mn}(\text{salen})_2]$ type molecules as single-molecule magnets (SMM) with metal-dithiolene complex as conducting parts (Figure 1) [2-4]. Although SMM units of these hybridized complexes exhibited paramagnetic behavior, their conductivities are very low. In this work, new hybridized complexes were prepared in order to improve their conductivities by the use of electrochemical crystallization of the precursor complexes. For example, dark brown plate like crystals of hybridized complex $[\text{Mn}(5\text{-MeO-saltmen})(\text{acetone})_2][\text{Ni}(\text{dmit})_2]_6$ (**1**) (Figure 1) can be obtained by electrolysis of acetone solution (15 ml) including $[\text{Mn}(5\text{-MeO-saltmen})][\text{PF}_6]$ (76 mg, 0.13 mmol) and $(\text{Bu}_4\text{N})[\text{Ni}(\text{dmit})_2]$ (20 mg, 0.028 mmol) for constant current (1 μA) at 20 $^\circ\text{C}$ for a week. Figure 2 shows packing diagram of **1**. The SMM units were formed by dimerization of the Mn complexes. Ferromagnetic exchange parameter J_F in the dimeric core (1.85 cm^{-1}) can be estimated by Mn-O distance (2.298 \AA) in the out-of-plane dimeric core. For conducting part, there are three crystallographically independent $[\text{Ni}(\text{dmit})_2]$ molecules. Columnar structure was formed by three fold staking of the molecules between the cation layers. In spite of the bulky cations, many intermolecular S...S contacts (3.546-3.679 \AA) shorter than van der Waals distance (< 3.7 \AA) were formed along the columns, as well as between the columns. Magnetic, electrical and other properties of various hybridized complexes including the crystal will be discussed.

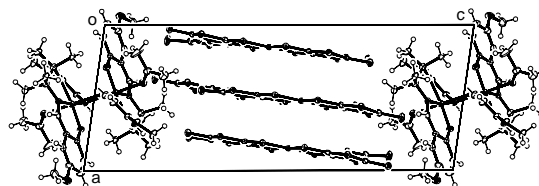
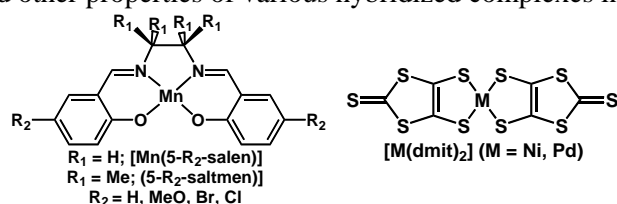


Figure 1 Components of the hybridized complexes.

Figure 2 Crystal structure of **1**.

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