Magnetic Phase Transitions in 2D Quadratic Magnets BBDTA•*X*

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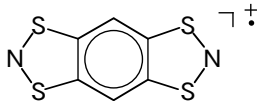
Cyclic thiazyl radicals exhibit strong intermolecular interactions via the characteristic S•••N and/or S•••S contacts between the molecules and easily form multi-dimensional networks in their solid state. Such properties as the spin-Peierls transition, magnetic ordering, room-temperature magnetic bistability, photoinduced phase transition, metallic conduction, negative resistance have been identified in these materials, which makes them highly attractive as building blocks of molecule-based magnetic materials.

We focus on the monocationic species (S = 1/2) of benzo[1,2-d:4,5-d']bis[1,3,2]dithiazole (BBDTA), whose molecular structure is presented in Scheme 1. We have systematically investigated the crystal structure and magnetic properties of BBDTA cation radical salts with various counter anions in search of new magnetic materials with a higher magnetic transition temperature. Recently we have found ferromagnetic ordering in the salts γ-BBDTA•$GaCl_4$ and BBDTA•$FeCl_4$ below 7.0 K and 44.5 K, respectively. In InX_4 (X = Cl, Br) derivatives, a one-dimensional coordination polymer structure was formed and the spin Peierls transition occurred at 108 K and 250 K, respectively. Thus, these cationic salts showed various crystal structures and magnetic phase transitions at relatively higher temperatures.



Scheme 1

In this presentation, we report crystal structure and magnetic properties of BBDTA•X salts (X = a-$GaBr_4$, $TlBr_4$, InI_4, TlI_4 and $AuBr_4$). These crystals comprised a stack of alternating $BBDTA^+$ cation assembled layers and tetrahalogenometalate anion layers. $BBDTA^+$ formed 2D quadratic magnetic networks via intermolecular S•••N, S•••S or S•••C interatomic contacts. The a-$GaBr_4$ and $TlBr_4$ salts showed antiferromagnetic phase transitions at 15.5 K and 11.8 K, respectively. In the InI_4 and TlI_4 salts metamagnetic phase transitions took place at 10.6 K and 8.9 K. On the other hand, the $AuBr_4$ salt showed a paramagnetic-to-diamagnetic phase transition at 44 K. We will discuss their detailed structure and magnetic behaviors and the origin of the magnetic difference.

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