[Sn8]6−-Bridged Mixed-Valence ZnI/ZnII in {[K2ZnSn8(ZnMes)]2}4− Inverse Sandwich-Type Cluster Supported by a ZnI–ZnI Bond

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Abstract
Since [Sn8]6− was discovered from the solid-state phase in 2000, its solution chemistry has been elusive due to the high charges and chemical activity. Herein, we report the synthesis and characterization of an inverse sandwich-type cluster dimer {[K2ZnSn8(ZnMes)]2}4− (1 a), in which the highly charged [Sn8]6− is captured by mixed-valence ZnI/ZnII to form the dimer {closo-[Zn2Sn8]}2 moieties bridged by a Zn-Zn bond. Such Zn-Sn cluster not only exhibits a novel example of mixed-valence ZnI/ZnII for stabilizing highly active anion species, but also indicates the [Sn8]6− cluster can act as a novel bridging ligand, like arene, with a η4:η4-fashion. Theoretical calculations indicate that a significant delocalization of electrons over Zn atoms plays a vital role in the stabilization of the [Sn8]6− species. The AdNDP and magnetic response analyses clearly showed the presence of local σ-aromaticity in three cluster fragments: two ZnSn4 caps and Sn8 square antiprism.

Author keywords
inverse sandwich
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[Sn8]6−