

# Ternary aromatic and anti-aromatic clusters derived from the hypophosphite species $[\text{Sn}_2\text{Sb}_5]^{3-}$

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## Abstract

Heterometallic clusters have attracted broad interests in the synthetic chemistry due to their various coordination modes and potential applications in heterogeneous catalysis. Here we report the synthesis, experimental, and theoretical characterizations of four ternary clusters ( $[\text{M}_2(\text{CO})_6\text{Sn}_2\text{Sb}_5]^{3-}$  (M = Cr, Mo), and  $[(\text{MSn}_2\text{Sb}_5)_2]^{4-}$ , (M = Cu, Ag)) in the process of capturing the hypophosphite  $[\text{Sn}_2\text{Sb}_5]^{3-}$  in ethylenediamine (en) solution. We show that the coordination of the binary anion to transition-metal ions or fragments provides additional stabilization due to the formation of locally  $\sigma$ -aromatic units, producing a spherical aromatic shielding region in the cages. While in the case of  $[\text{Mo}_2(\text{CO})_6\text{Sn}_2\text{Sb}_5]^{3-}$  stabilization arises from locally  $\sigma$ -aromatic three-centre and five-centre two-electron bonds, aromatic islands in  $[(\text{AgSn}_2\text{Sb}_5)_2]^{4-}$  and  $[(\text{CuSn}_2\text{Sb}_5)_2]^{4-}$  render them globally antiaromatic. This work describes the coordination chemistry of the versatile building block  $[\text{Sn}_2\text{Sb}_5]^{3-}$ , thus providing conceptual advances in the field of metal-metal bonding in clusters. © 2021, The Author(s).