Glenn T. Seaborg Center Postdoctoral Candidate Seminar

Structure, Reactivity and Solution Dynamics of Nonastannide Zintl ion; Sn_9^{4-}

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Building 70A, Room 3377

Since their discovery in 1890's, nine-atom group-14 Zintl ions have exhibited rich chemistry in both gas and condensed phases. In particular, the solution reactivities of the E_9^{4-} ions (E= Si, Ge, Sn, Pb) with different reagents have resulted in many discoveries of their chemical properties such as functionalization, formation of oligomers, exchange of vertices, reactivity with transition metals, and more recently, reactivity with lanthanides.

This presentation mainly focuses on solution reactivity of Sn_9^{4-} ion with transition metal atoms and with electrophiles. The Sn_9^{4-} anion is obtained from its solid state intermetallics, such as K_4Sn_9. It is soluble in polar solvents such as liquid ammonia and ethylenediamine. We showed that in ethylenediamine (en) Sn_9^{4-} ion is a very strong Brønsted base that deprotonates en to form the Sn_9H^{3-} ion. The diamagnetic Sn_9H^{3-} ion was mischaracterized as the Sn_9^{3-} paramagnetic radical in numerous publications since 1983. Our results show a strong contrast to these earlier studies.

In our studies, we isolated several new cluster ions. $M@Sn_9R^{3-}$ (M= Ni, Pd, R= H, $SnCy_3$) clusters are endohedral ions with *exo*-substituted groups. We prepared the $Pd@Sn_9PdSnCy_3^{3-}$ ion from a new type of reaction, where the Pd metal is oxidatively inserted into the *exo*-bond of $Pd@Sn_9$–$SnCy_3$. Finally, we isolated the largest-known deltahedral cluster to-date, $Pd_2@Sn_{18}^{4-}$, from Sn_9^{4-} and $Pd(PPh_3)_4$ precursors.

In addition to synthesis and isolation of these clusters, we studied their highly dynamic nature by ^{119}Sn, ^{1}H spectroscopy. The Sn_9R^{3-} ions (R= H, $SnCy_3$) and $M@Sn_9R^{3-}$ ions (M= Ni, Pd and R= H, $SnCy_3$) exhibit fast intramolecular exchange of the all 9-Sn atoms, while the *exo*-substituent groups scramble around the clusters. On the other hand, the Sn_9-$^{i}Pr^{3-}$ ion has non-mobile alkyl substituent, which removes the *exo*-bonded Sn atom from exchanging with the remaining 8-Sn atoms of the cluster.

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