

Transition Metal Derivatives of Naked
Post-Transition Element Clusters

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Many new developments have occurred in recent years in the area of anionic post-transition metal clusters, the so-called "Zintl ions" [1]. Some of the most recent work in this field has dealt with developing transition metal derivatives of these clusters. Two examples are in Figure 1. These compounds are of interest because of their novel structural and bonding modes and may show promise as precursors to useful solid-state materials, such as transition metal chalcogenides.

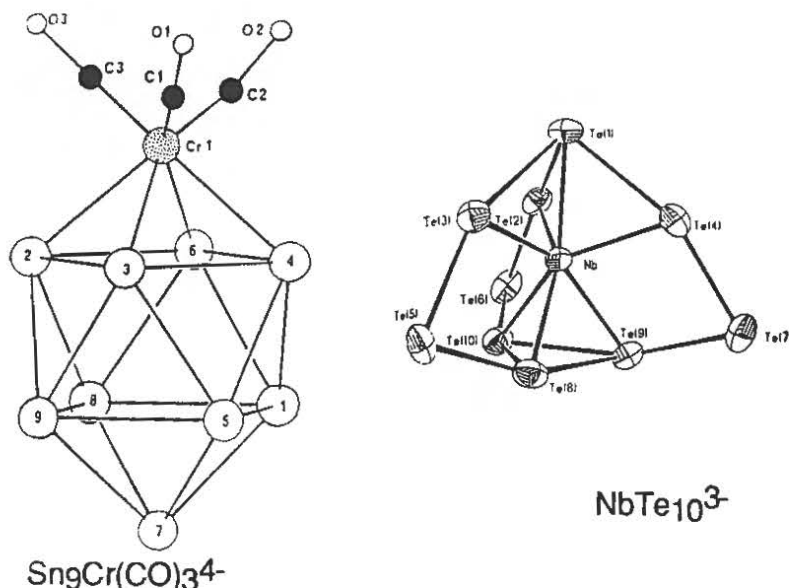


Figure 1.

Zintl Ions are polyatomic anions of the post-transition elements of groups 13-16 [1]. Homoatomic and heteroatomic anions are known; examples include Pb_5^{2-} , Sb_7^{3-} , and $\text{Tl}_2\text{Te}_2^{2-}$ [1]. The first evidence for these compounds was discovered by Joannis [2a], who noted in 1891 that Na-NH_3 solutions turned a deep green color upon the addition of lead. Extensive electrochemical studies by Zintl [2b] and others [2c] on ammonia solutions of extracted intermetallic alloys established the presence of polyatomic anions. Isolation of these anions resisted all efforts until 1970, when Kummer and Diehl [3] obtained crystals of $\text{Na}_4(\text{en})_7\text{Sn}_9$, where en = ethylene diamine. Unfortunately, the resulting crystal structure was disordered. In 1975, Corbett et al. [4] succeeded in isolating Sb_7^{3-} and other anions by using a macrocyclic ligand (2,2,2-crypt) to sequester the countercation. The ligand presumably prevents electron transfer from the strongly reducing polyanion back onto the cation, stabilizing the anion relative to an intermetallic solid phase. As a result of this success, Corbett was able to develop a synthetic methodology which has proven useful for the synthesis of a large number of Zintl anions. Typically, an intermetallic alloy such as NaSn is extracted in an amine of similar solvent in the presence of crypt. Crystallization from these solutions yields deeply colored, exceedingly air sensitive solids with the composition $(\text{crypt-M}^+)_n\text{E}_q^{n-}$, where M is an alkali metal, and E is a post-transition element [1].

A large number of structural studies have been carried out on Zintl anions by Corbett and other workers [1]. Some of the more interesting Zintl anions have polyhedral cluster geometries [Figure 2]. The solution behavior of these compounds has been studied by a number of physical techniques, including Mössbauer, EXAFS, multinuclear NMR, and potentiometry [1]. In particular, multinuclear NMR has proven very useful in characterizing species in solution which are otherwise unisolatable, such as the series of mixed clusters $\text{Ge}_{(9-x)}\text{Sn}_x^{4-}$ studied by Rudolph et al. [5].

Much of the recent work in the Zintl ion field has been concerned with the synthesis of transition metal and organometallic derivatives of Zintl anion clusters. This work may be broken into two groups: 1) Mixed post-transition element/transition metal clusters. 2) Clusters derived from polyhedral Zintl ions.

A number of mixed post-transition element/transition metal clusters have recently been synthesized. Many of these compounds have unprecedented and novel structures. Examples include $\text{KAu}_9\text{Te}_7^{4-}$ [6], $\text{Mo}_4\text{Te}_{16}(\text{en})_4^{2-}$ [7], RbNbAs_8^{3-} [8], NbTe_{10}^{3-} [9], and CrTe_{24}^{4-} [10]. Many of these compounds are obtained fortuitously and quite unexpectedly from reactions of Zintl anions with transition metals.

Clusters derived from polyhedral Zintl ion frameworks are rare. Rudolph et al. obtained NMR evidence for species obtained by reactions of Sn_9^{4-} , Pb_9^{4-} , and TlSn_8^{5-} with $\text{Pd}(\text{PPh}_3)_4$ or $\text{Pt}(\text{PPh}_3)_2$ in en [11]. Whitmire et al. have reported the structure of the $[\text{Bi}_4\text{Fe}_4(\text{CO})_{13}]^{2-}$ anion, a derivative containing a Bi_4^{4-} tetrahedron [12]. More recently, Haushalter et al. have characterized $\text{Sn}_9\text{Cr}(\text{CO})_3^{4-}$ [13] and $\text{As}_7\text{Cr}(\text{CO})_3^{3-}$ [14]. The first compounds may be thought of as a nido- Sn_8^{4-} cluster which is capped with a $\text{Cr}(\text{CO})_3$ fragment. The As_7 fragment in $\text{As}_7\text{Cr}(\text{CO})_3^{3-}$ bears a striking resemblance to the norbornadiene ligand in $\text{PdCl}_2(\text{norbornadiene})$.

The chemistry of post-transition element clusters, especially that of transition metal derivatives, is in its infancy. Future work promises to discover a myriad of new structural and bonding modes of the post-transition elements.

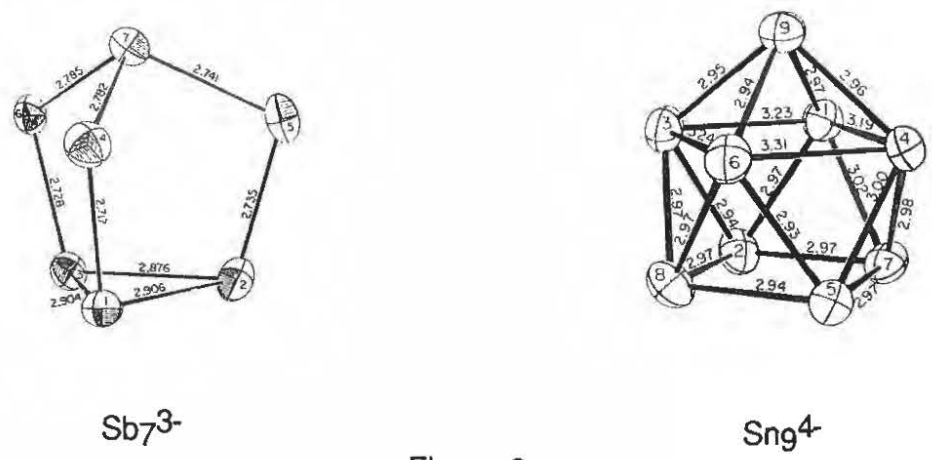


Figure 2.

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