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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.

Zintl ions are polyatomic anions of the post-transition elements of groups 13-16 [1]. Homoatomic and heteroatomic anions are known; examples include Pb32-, Sb73-, and Tl2Te25- [1]. The first evidence for these compounds was discovered by Joannis [2a], who noted in 1891 that Na-NH3 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 Na4(en)7Sn9, where en = ethylene diamine. Unfortunately, the resulting crystal structure was disordered. In 1975, Corbett et al. [4] succeeded in isolating Sb73- and other anions by using a macrocyclic ligand (2,2,2-crypt) to sequester the counteranion. 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 (crypt-M+)nEaq-, where M is an alkali metal, and E is a post-transition element [1].

Figure 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 com-
ounds 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 clus-
ters. This work may be broken into two groups: 1) Mixed post-transition ele-
ment/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], $\text{RbNbAs}_{3}^{3-}$ [8],
$\text{NbTe}_{10}^{3-}$ [9], and $\text{CrTe}_{2}\text{H}_{2}^{4-}$ [10]. Many of these compounds are obtained fortui-
tously 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 $\text{Sn}_{9}^{4-}$, $\text{Pd}_{9}^{4-}$, and
$\text{TlSn}_{8}^{5-}$ with $\text{Pd(PPh}_{3})_{4}$ or $\text{Pt(PPh}_{3})_{4}$ in en [11]. Whitmire et al. have reported the
structure of the $[\text{Bi}_{4}\text{Fe}_{4}(\text{CO})_{11}]^{2-3}$ anion, a derivative containing a Bi$_4$ tetrahedron
[12]. More recently, Haushalter et al. have characterized $\text{Sn}_{9}\text{Cr(CO)}_{11}^{4-}$ [13] and
$\text{As}_{7}\text{Cr(CO)}_{3}^{3-}$ [14]. The first compounds may be thought of as a nido-$\text{Sn}_{9}^{4-}$ cluster
which is capped with a $\text{Cr(CO)}_{3}$ fragment. The $\text{As}_{7}$ fragment in $\text{As}_{7}\text{Cr(CO)}_{3}^{3-}$ bears a
striking resemblance to the norbornadiene ligand in $\text{PdCl}_{2}(\text{norbornadiene})$.

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


   (c) These and other articles on early Zintl ion chemistry may be found in "Metal Ammonia Solutions," Jolly, W., Ed.; Dowden, Hutchinson, and Ross: Stroudsburg, PA 1972.


