Polyatomic Zintl Anions of the Post-Transition Elements

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I. Introduction

In the simplest world, metals are oxidized only to monoatomic cations and nonmetals are reduced to simple anions while the so-called metalloids might do both, or neither. However, chemists now recognize that the real world is not so elementary. First, it has become increasingly clear that the conversion of many main-group elements to such simple ions or compounds often go through polyatomic network, chain, cluster, or ring intermediates in which limited homoatomic bonding represents a retention to some degree of the bonding characteristics of the element. This is especially true for nonmetals like boron and phosphorus where polyatomic intermediates clearly represent the stepwise breakup of the structure of the element.[2] Furthermore, such polyatomic ions are generally more stable than analogous neutral species like Sb_4 and Bi_4 since disproportionation rather than a simple rearrangement is required for the ions to attain the normal state of the element.[3] Second, the description *metal*, *metalloid*, or *non-metal* for the elements of interest refers to properties, mainly optical and conduction, of the condensed elemental solids, and these labels are not particularly good predictors regarding the ease of oxidation or reduction or the tendency toward homoatomic bonding in small units under other conditions.

Given this foresight, one is then ready to deal with cluster anions formed by what are nominally metals in the elemental state together with polycations that form from nonmetals. In these cases one recognizes that the electronic "rules" of stability are now those pertinent to bonding in clusters, rings, etc., and these may have little to do with the elemental structures. Isoelectronic series will now be recognized, some with the elements such as $Si_4^{4-} \triangleq$ (is equivalent to) P_4, some that are isoelectronic only with midpoints in the elemental scheme, e.g., $Bi_4^{2-} \triangleq Te_4^{2+}$, and others that are even wider ranging, $Pb_5^{2-} \triangleq$ "Pb_2Bi_3" $\triangleq Bi_5^{3+} \triangleq C_2B_3H_5$. By and large, the pertinent electronic rules are both well-known and diversely formulated, and only a few examples will require extra explanation. Fortunately for synthetic chemists, their abilities to discover still well exceed the theorists' capabilities to predict, presumably because relatively subtle factors determine stability or nay. The most interesting and novel examples are often the more electron poor, generally those with 2.2 to ~3.0 p electrons per average cluster element. Even more orbitally rich clusters of the transition metals like $Nb_6Cl_{12}^{2+}$ and $Mo_6Cl_8^{4+}$ represent quite separate and distinct subjects.[4]

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This review will deal primarily with the homopolyatomic anion examples that have been labeled[5] as Zintl ions. This recognizes the earliest systematic investigator of their solution chemistry who first identified many such species following the reaction of either intermetallics formed between alkali metals and certain post-transition elements or the separate elements with liquid ammonia. Polyatomic cation examples that are often isoelectronic are notably less abundant for a variety of reasons. The principal activity following an earlier review on the polycations[3] has involved a confirmation of the predicted structure of Bi_8^{2+} [6] and further results on polychalcogenide clusters[7,8] where electronic and structural configurations related to Zintl

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anions are not very common. The present review will limit its attention principally to polyanionic clusters and rings that require some unusual care or conditions for their stabilization. Complexing of the countercation or the use of nonaqueous solvents are the most common means to stabilize these.

Obviously, polyatomic anions related to "natural" anions—polysulfides, selenides and iodides, for example—are not germane to this article. In addition, nearly all of the pertinent chemistry involves the post-transition, as opposed to main-group, elements. Much of the polysilicon and polyphosphorus chemistry is relatively unrelated, witness for example the existence of the polysilanes and phosphanes and the absence of simple ions. An extensive and fascinating polyphosphide anion chemistry has been developed and reviewed elsewhere.[2] On the other hand, the chemistries of some polygermanium, arsenic, and tellurium ions are more related, and these will be briefly noted where germane. A natural extension of the Zintl anion examples has also led to more recent discoveries of heteroatomic cluster anions, some of which represent likewise novel configurations and electronic states. However, some of the latter examples bridge directly to classical, centered polyanions, and these will receive attention only to the (somewhat arbitrary) degree that chemists might be inclined to view their existence and bonding as unusual.

Most of the Zintl ions and their relatives to be considered here have been prepared and isolated by relatively straightforward solution techniques, the means of stabilization and the results being the novel features. Brief note will also be made of what is probably the "next frontier" in this area, the relatively large and often different group of polyatomic cluster and infinite "anions" that can be found and studied apparently only in the solid state in intermetallic phases such as Na_4Sn_4, $Li_{12}Si_7$, and K_3Ga_{13}. The electronic regularities and classifications in some of these are more difficult to perceive, and the novelty and prospects for interesting science are correspondingly larger.

II. Background

The first evidence for what are called Zintl ions was reported by Joannis in 1891[9] from studies of the reaction of sodium in liquid ammonia with a variety of metals. He observed that the reaction of the characteristic blue solution of sodium with excess lead gave new solids which colored the ammonia an intense green. More attention was given to the precipitates which were found to have the compositions $NaPb_4$ or $NaPb_2$ depending on conditions.[10] A brown solution from the reaction of sodium with excess antimony was also noted.

Kraus[11] was the first to study the green sodium–lead solution, showing that it was an electrolyte with the green color associated with the anion. He also observed that the lead solute would plate out on an anode and form at a lead cathode, that the lead solute could be precipitated on addition of normal lead(II) salts, and that tin showed similar reactions with sodium solutions. There appeared to be about two lead atoms per charge according to Faraday's law studies, leading to the formulation $NaPb_2$ for the solute. Later, more thorough measurements by Smyth[12] showed that an average of 2.26 Pb per Faraday plated out on the anode from the saturated solution. Similarly, a maximum of 2.24 lead atoms per Na was found to dissolve in NH_3 solutions, which was interpreted in terms of an equilibrium between $NaPb_2$ and $NaPb_3$ solutes. A related study by Beck[13] yielded maximum solubilities of 4.0 Te/Na and 2.33 Sb/Na, the latter value decreasing appreciably on dilution (probably because of the presence of two species). These observations led Kraus[14,15] to speculate that the polyanionic salts in equilibrium with the metals (assuming single solute species) were $Na_4Pb{\cdot}Pb_8$, $Na_3Sb{\cdot}Sb_6$, and $Na_2Te{\cdot}Te_3$ and that as electrolytes they contained the anions Pb_9^{4-}, Sb_7^{3-}, and Te_4^{2-}, respectively.

The next information on these anions came from extensive systematic studies by Zintl and co-workers that were published in the 1930s.[16-19] Zintl recognized that these solutions came about for what could be viewed as "polar" intermetallics,[14,16] the more electronegative members of these lying close to the metalloid elements. X-ray diffraction was becoming available at this time as an invaluable aid for sorting phases as well as for structural investigations of the intermetallic phases. Zintl was also a pioneer in determining the structures and properties of such polar intermetallics, which have been subsequently labeled "Zintl phases"[20] (section IX), and so the solution of many of the same materials in liquid ammonia seemed particularly relevant to him. However, subsequent research by Zintl and, more so, by others has shown that virtually none of the clusters or groupings later postulated or isolated as Zintl ions are discernible in the structures of appropriate intermetallic phases although the M^ISn and M^IPb phases were later found to contain tetrahedra of the heavy metal.[21,22]

The first investigations reported by Zintl and coworkers[16] were potentiometric titrations; conductance measurements were also employed in a few cases but these were relatively uninformative. Since reactions of the elements with sodium solutions were sometimes relatively slow, they instead titrated a sodium solution in NH_3 with one of a normal-valent salt of the metal. Thus, the first PbI_2 added would be reduced to the metal which then would redissolve (be reduced) relatively rapidly. The potentiometric measurements thus followed the measured oxidation of the sodium and, subsequently, of any polylead anions until a permanent precipitate of lead occurred. The reaction in the earlier stages could be described as

$$(4 + 2x)\mathrm{Na} + x\mathrm{PbI_2} \rightarrow \mathrm{Na_4Pb}_x + 2x\mathrm{NaI}$$

A reference electrode was usually established early in the oxidation sequence by filling a relatively isolated compartment with a small amount of the solution.

The course of two potentiometric and one conductometric titrations in the lead system is reproduced in Figure 1 from Zintl's original article. The compositions of the indicated ions were generally quite well marked by the data, i.e., in four experiments they obtained $x = 6.89$ and 7.02 for Pb_7^{4-} and $x = 8.86$–9.11 (average 8.96) for Pb_9^{4-}. The former composition was seen only with the more dilute sodium solutions, as might be expected for a concentration-dependent equilibrium. However, ion pairing may have a significant effect as well since the more reduced ion was not seen in a comparable study with potassium. Stable emf's could not be obtained with tin solutions. Similar experiments

Table I. Polyanions Deduced by Zintl in Liquid Ammonia[a]

		As_3^{3-}	yellow	Se_2^{2-}	bright red
		As_5^{3-}	dark red-brown	Se_3^{2-}	wine red
		As_7^{3-}		Se_4^{2-}	green
				$Se_{5,6}^{2-}$	red-green (dichroic)
Sn_9^{4-}[b]	blood red	Sb_3^{3-}	deep red	Te_2^{2-}	violet
		Sb_7^{3-}[b]	red·brown	Te_3^{2-}	
				Te_4^{2-}	dark red
Pb_7^{4-}	green	Bi_3^{3-}	deep violet		
Pb_9^{4-}	green (to violet)	Bi_5^{3-}	brown		
		Bi_7^{3-}[b,c]	red·brown		

[a] Polysulfides omitted. [b] From extraction studies only. [c] See text regarding composition.

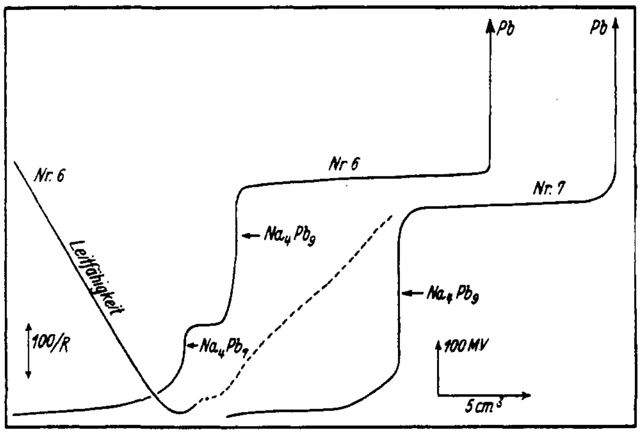


Figure 1. The potentiometric and conductometric titration of sodium in liquid ammonia with a lead iodide solution according to Zintl, Goubeau, and Dullenkopf. Reproduced with permission from ref 16. Copyright Buchexport, 1931.

with Cu, Ag, Au, Zn, Cd, Hg, or Tl iodides in ammonia solution indicated the absence of a significant anion solution chemistry for these elements.

In order to secure pure solutions relatively directly and rapidly, Zintl, Harder,[17] and Dullenkopf[18] also investigated the direct solution of binary alloys and their mixtures into ammonia. Extraction of compositions (Sn, Pb)/Na = 2.25 to ~2.75 gave evidently pure solutions and excellent analyses for the indicated homoatomic M_9^{4-} compositions. Colloidal particles were also seen in the solutions, presumably from alloy disintegration or peptization. The composition NaSb readily yielded a saturated solution analyzing $NaSb_{2.33}$ ($Na_3Sb_{6.99}$) while the composition $NaBi_{1.95}$ (= $Na_3Bi_{5.85}$) was obtained only after extraction of a $NaBi_3$ alloy for several months. It was presumed that the latter represented an unsaturated solution, and so the result was rounded up to Na_3Bi_7 (rather than the closer Na_3Bi_6) for the following reasons: The composition Na_3Bi_5 had already been deduced by titration experiments described above, all the other main group 5 anions appeared to have a charge of 3− (or a multiple thereof), basically the 8 − N rule (below), and all of the polyanions they had found appeared to contain an odd number of heavy atoms. As will be seen later, present evidence suggests this train of reasoning was probably in error and that the correct species may have been $Na_2Bi_{3.9} \simeq Na_2Bi_4$.

The ions so deduced in liquid ammonia by these investigators are summarized in Table I along with the indicated colors except that the less relevant polysulfide results have been omitted. In addition, the unlisted valence compounds Na_3M^{V} and Na_2M^{VI} usually precipitated in the early stages of oxidation of the sodium solutions. The violet color noted with what was presumed to be Pb_9^{4-} pertained to the rubidium and cesium systems, perhaps another hint of ion-pairing effects.

The Pb_9^{4-} species produced electrolytically was observed to be unstable when a Et_4NI electrolyte was used. None of the characteristic green color of this ion was observed with a SrI_2 electrolyte or on extraction of a $CaPb_3$ composition. Although the Sn_9^{4-} solutions could not be readily achieved by electrolysis, this and the lead analogue were also obtained in a disproportionation reaction following Bergstrom,[23] viz.

$$11Sn + 6KNH_2 \xrightarrow{NH_3} K_4Sn_9 + 2KSn(NH_2)_3$$

Germanium gave only negative results in all of these experiments although extraction of an NaGe composition for several days gave a faint brown color in the ammonia and a qualitative test for that element in the brown residue. Corresponding reactions with Na–Ga, Na–In, Cs–Ga, Cs–In, and Cs–Tl alloys yielded negative results.

Evaporations of the metal-saturated polylead, -tin, -antimony, and -bismuth solutions at low temperatures all gave dark, non-metallic-appearing and evidently amorphous solids that were apparently the $Na(NH_3)_n^+$ salts of the indicated anions. Removal of NH_3 by pumping went through several intermediate ammoniates to give gray, often pyrophoric, products that eventually took on a metallic reflectance. Two ammoniates were specifically shown to be amorphous to X-rays while the ammonia-free products in all cases were clearly the appropriate binary metal compounds or their mixtures. Typical decompositions could thus be described as

$$(Na(NH_3)_n^+)_4Pb_9^{4-} \rightarrow 4NaPb_{2.25} + 4nNH_3$$

or

$$(Na(NH_3)_n^+)_3Sb_7^{3-} \rightarrow 3NaSb + 4Sb + 3nNH_3$$

where the indicated Na–Pb composition lies within a homogeneity range of the $NaPb_{3-x}$ (Cu_3Au-type) phase. The production of only known and unrelated intermetallic phases by this route is general. The solution compositions Na_3Sb_3 and Na_3Bi_3 are of course the same as the one-to-one phases known in the binary intermetallic systems but these must be different; NaSb contains infinite helical chains of antimony that are isoelectronic with elemental tellurium.

The bonding interpretations purposed for these anion structures at that time are naturally no longer very appropriate. Analogies with the polysulfides were strongly featured as well as the fact that the apparent charges on all of these (Table I) appeared to follow the

Table II. Homopolyatomic Zintl Anions of Known Structure[a]

anion	symmetry	characteristics	p electrons	str ref	isoelectronic analogues
Ge_9^{2-}	C_{2v} ($\sim D_{3h}$)	dark red rods	20	34	$B_9H_9^{2-}$ [b,c]
Ge_9^{4-}	C_{4v}		22		Bi_9^{5+} (D_{3h})[d]
Sn_9^{4-}	C_{4v}	dark red rods	22	38	Bi_9^{5+} (D_{3h})
Sn_9^{3-}	D_{3h}	dark red plates	21	39	
Sn_5^{2-}	D_{3h}	orange-brown plates	12	40	Bi_5^{3-} [c,e]
Pb_5^{2-}	D_{3h}	ruby red prisms	12		
Sb_4^{2-}	D_{4h}	dark red wedges	14	41	Te_4^{2+},[f] Se_4^{2+} [g]
Bi_4^{2-}	D_{4h}	dark green prisms or plates	14	43	
As_{11}^{3-}	$\sim D_3$	deep red rods	36	44	P_{11}^{3-} [h]
Sb_7^{3-}	C_{3v}	brown prisms, rods	24	41,45	As_7^{3-} [i]

[a] Crypt·K^+ or crypt-Na^+ cations. [b] Reference 35. [c] Reference 36. [d] Reference 37. [e] Burns, R. C.; Gillespie, R. J.; Luk, W.-C. *Inorg. Chem.* 1978, *17*, 3596. [f] Reference 42. [g] Reference 8. [h] Wichelhaus, W.; von Schnering, H.-G. *Naturwissenschaften* 1973, *60*, 104. [i] Reference 46.

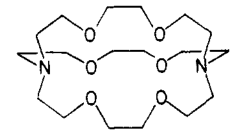
$8 - N$ rule for the corresponding hydrides. The solutes were accordingly formulated as adducts of the sodium salts of the hydrides, e.g., $Na_4Pb{\cdot}Pb_8$, $Na_3Bi{\cdot}Bi_4$, and $Na_2Te{\cdot}Te_3$, analogous to Kraus' interpretations. The relationship of these phases to a salt–metal transition seen in the solid state in some binary systems as a function of composition also received considerable attention.

The literature suggests there was negligible subsequent activity in this area for nearly four decades. Of course, negative results are seldom published. An apparently related phenomenology concerned the solution of some of the same intermetallic phases in molten salts. This behavior was first studied in Zintl's time in NaBr by Heyman and Weber[24] and more recently in the lower melting NaCl–NaI eutectic by Okada et al.[25] The latter found that sodium alloys of Au, Pb, and Sn are measurably but only slightly soluble, usually ≤1 mol %, while the corresponding antimony and bismuth phases are notably more soluble. Solutions of the less relevant valence compounds Na_3Sb and Na_3Bi cryoscopically appear to represent the simple salts although the latter is metallic in the solid state. Most interesting is the phase NaSb which dissolves to a few percent and cryoscopically behaves as Sb_3^{3-} quite well and hence as a Zintl ion (Table I), in contrast to the structure of the solid alloy which, again, contains infinite antimony helices. Observation of other possible Zintl anion species is presumably limited by their thermal instabilities at the melt temperatures involved (≥570 °C in the above cases).

III. Isolation of Zintl Anions

The isolation of any solid derivatives of the Zintl anions has only been accomplished in the last 15 years. Kummer and Diehl[26] obtained the first example in the compound $(Na)_4(en)_7Sn_9$ (en = ethylenediamine). They found the alloy composition $NaSn_{2.4-2.5}$ slowly dissolved in en (or other polyamines) on warming, and the indicated compound could be precipitated on the addition of monoglyme or THF. The reddish brown product was strongly diamagnetic and gave a single, broad ^{119}Sn Mössbauer resonance at +0.15 mm^{-1} s^{-1} vs. α-Sn with a half-width of 1.90 mm s^{-1}. Additional examples of Zintl's "polyanionic salts" later reported were the copper-colored $Na_4(en)_5Ge_9$ and the dark red $Na_3(en)_4Sb_7$ which were isolated with similar techniques and likewise identified by elemental analyses.[27-29] The former slowly loses en at room temperature. A salt of the lead anion could not be isolated. A subsequent, incomplete crystal structure study of the above tin compound[28,29] identified a distorted and evidently somewhat disordered Sn_9 polyhedron therein, but the en molecules could not be located well (R = 11.7%, Mo Kα, $2\theta \le 30°$). We will return to the geometric features of this anion in a later comparison with other Sn_9 polyhedra that have been structurally identified.

A more general solution to the isolation of diverse examples of Zintl anions lay in the use of a more effective sequestering agent for the countercation. The all-too-ready reversion of this type of salt to an intermetallic phase can be viewed as the result of delocalization of electrons from the Zintl polyanions—usually very good reducing agents—back onto the cations. Blocking this pathway thus promises some stabilization. Although quaternary ammonium cations do not appear sufficiently stable to reduction by some of the anions (below), good complexing agents for the cations prove very useful. The selection of the macrocyclic ligand 1,



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abbreviated 2,2,2-crypt or hereafter just crypt,[30,31] was guided by the reports by Dye and co-workers that this octadentate agent not only greatly enhanced the solubility of the alkali metals themselves in various solvents[32] but also allowed the isolation of the remarkable (crypt–Na^+)Na^-.[33] Its presence was found not only to greatly increase the rate of solution of many intermetallic phases, especially in en and to a lesser extent in NH_3, but also to allow the ready isolation of many salts containing the Zintl anions, for example

$$2KPb_{2.5} + 2(2,2,2\text{-crypt}) \xrightarrow[50\ °C]{en} (2,2,2\text{-crypt-}K^+)_2Pb_5^{2-}$$

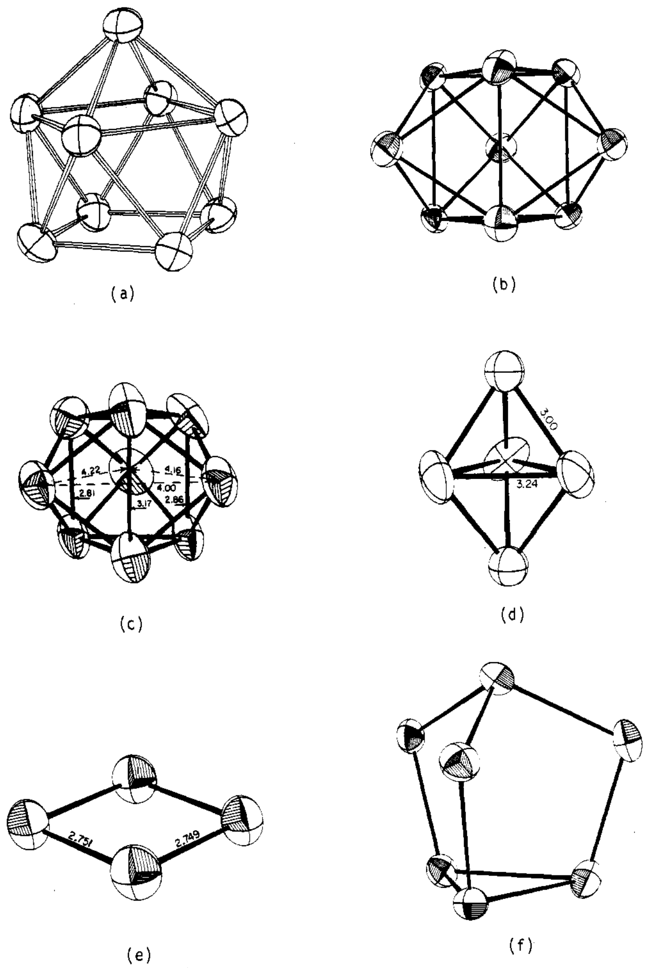
Table II lists the principal homoatomic anions that have been so obtained and characterized by single-crystal X-ray means together with some isoelectronic analogues.[34-46] Though 2,2,2-crypt is ideal for an ion the size of K^+, it works quite well with Na^+ as well. In this connection, it has been observed[47] that crypt–K^+ phases tend to enclose more nonbonded en solvent whereas the sodium analogues are more apt to be solvent-free and in a higher symmetry cell. Large cations of these types often dominate the crystalline packing and sometimes allow for the disorder among the anions or provide poor selectivity at a given site. Synthetic explorations with 2,2,1-crypt–Na$^+$ or 2,1,1-crypt–Li$^+$ (the numbers identify the ether oxygens in each chain) have generally been less productive; these reagents generally need to be handled as solutions, and they tend to yield oils, tars, etc. rather than crystals, in part perhaps because of crypt reduction.[47]

Comparison of the polyatomic anions that have been isolated and characterized structurally (Table II) with those detected by Zintl (Table I) reveals many differences. The possible identity of the isolated Bi_4^{2-} and the analyzed $Bi_{5.85}^{3-}$ (= $Bi_{3.90}^{2-}$) was noted earlier. Some of Zintl's ions have been subsequently isolated by fairly conventional means, for example, the barium salt of As_7^{3-} by more direct, high-temperature reactions.[46] Even for tellurium where the stability of polyanions might be the most borderline among the chalcogenides Te_3^{2-}, Te_4^{2-}·2MeOH, Te_5^{2-}, and the novel $\frac{1}{\infty}[Te_4Te_{2/2}^{2-}]$ have all been isolated.[48-51] All of the polychalcogenide anions obtained in solution appear to be simple chain fragments and will not be considered further.

Some ions reported by Zintl and not yet isolated involve higher charges per atom than in species obtained to date (Table II), As_3^{3-}, Sb_3^{3-}, Bi_3^{3-}, As_5^{3-}, and Bi_5^{3-}, for example, and their preparation in solid compounds may require either a solvent with a higher dielectric constant or a solvent or crypt-like agent that is more stable to reduction. (Some of the alloys studied reduce en to some degree with the evolution of hydrogen, more so for those with higher alkali-metal content, and the same is to be expected for certain solutes. This alloy oxidation can be useful in generating finely divided and more reactive heavy elements.) Mixed element clusters are also a useful means for reducing cluster charge (below). The dependence of results on solvent has generally not been well explored.

One of the surprises in Table II is the absence of any salt of Pb_9^{4-} even though this was the first such polyanion discovered. Dark brown or brown-green solutions are readily obtained with crypt in en from phases near the compositions $M^IPb_{2.2}$ (M = Na, K), but only the starting alloy with the obviously very stable M^IPb_{3-x} structure is recovered on solvent evaporation. The use of heat or of more sodium-rich alloys provides salts of the lower charged Pb_5^{2-} which, it will be noted, has very nearly the same composition ($Pb + Pb_9^{4-} \rightarrow 2Pb_5^{2-}$). The more familiar green solution is obtained from $M^IPb_{2.2}$ and crypt in ammonia, but again only the Pb_5^{2-} products can be isolated therefrom.[40] No reaction occurs with the alternative $SrPb_3$. Likewise, a dark brown solution is obtained by extraction of $NaPb_{2.25}$ with en alone, but only the original alloy precipitates on solvent evaporation or on the addition of monoglyme.[27] According to cryoscopic and conductometric measurements, Na_4Sn_9 and Na_4Ge_9 are hardly dissociated in en, even in dilute solution,[29] perhaps accounting for some of the color differences seen for the lead anion. The simpler Pb_5^{2-} ion, or any other polylead ion except Pb_9^{4-} for that matter, has not been detected in appreciable amounts in NMR studies on en solutions (below).

Although Na–Si alloys show no trace of solution in en or NH_3 alone, the addition of crypt to the latter gives dark green-brown solutions, and thin yellow to brown crystals can be obtained on very slow solvent evaporation at low temperatures. However, these are not stable for long at room temperature, and no structure solution (or analysis) has been attempted.[52] Although negative results are obtained with crypt and alkali-metal alloys of mercury or thallium, an interesting product is obtained with those of gold. In the presence of crypt, K–Au alloys dissolve in NH_3, and a white solid containing crypt and the alloy components can be recovered on evaporation of solvent at low temperatures. This product, which decomposes above −10 °C to produce metallic gold, has tentatively been suggested to be (2,2,2-crypt–K$^+$)Au$^-$ containing the $5d^{10}$ $6s^2$ pseudohalide anion Au$^-$.[53] The presence of a monoatomic gold anion in the (crypt–M$^+$)Au$^-$ compounds (M = K–Cs) has been given strong support by a recent Mössbauer study at low temperature which reveals a single gold resonance at 7.5–8.3 mm s^{-1} relative to pure gold.[54] (The yellow, semiconducting CsAu gives the same shift.) An Au_x^- anion has also been generated and studied in liquid ammonia alone.[55]



(a) (b) (c) (d) (e) (f)

Figure 2. Some homopolyatomic Zintl anion structures established by X-ray crystallography: (a) Sn_9^{4-}, (b) Sn_9^{3-}, (c) Ge_9^{2-}, (d) Pb_5^{2-}, (e) Bi_4^{2-}, (f) Sb_7^{3-} (50% probability thermal ellipsoids; references in Table II).

A collection of some of the anion structures determined by single-crystal X-ray studies of these phases is shown in Figure 2, namely, for Sn_9^{4-}, Sn_9^{3-}, Ge_9^{2-}, Pb_5^{2-}, Bi_4^{2-}, and Sb_7^{3-}, all of which represented new homopolyatomic anion configurations and several, the first of a kind: the Sn_9^{4-} unicapped antiprism, the Pb_5^{2-} trigonal bipyramid, and Sn_9^{3-}, a paramagnetic example. Most of these will be considered later along with additional physical measurements, cluster bonding regu-

Table III. Heteroatomic Zintl Anions of Known Structure Stabilized with Crypt

anion	symmetry	p electrons	str ref	isoelectronic analogues
$Sn_2Bi_2^{2-}$	$\sim T_d^{\,a}$	12	56	Sb_4, Bi_4 [b]
$Pb_2Sb_2^{2-}$	$\sim T_d^{\,a}$	12	57	
$Tl_2Te_2^{2-}$	C_{2v}	12	53	
$TlSn_8^{3-}$	C_{2v} ($D_{3h}^{\,a}$)	20	58	Ge_9^{2-} [c]
$TlSn_9^{3-}$	C_{4v} ($D_{4d}^{\,a}$)	22		$B_{10}H_{10}^{2-}$ [d,e]
$As_2Se_6^{3-}$	$\sim C_{2h}$	32	59	
$As_2Te_6^{3-}$	$\sim C_{2h}$	32	60	

[a] Configuration neglecting heteroatom. [b] Kohl, K. J.; Uy, O. M.; Carlson, K. D. *J. Chem. Phys.* **1967**, *47*, 2667. [c] Reference 34. [d] Schwalbe, C. H.; Lipscomb, W. N. *Inorg. Chem.* **1971**, *10*, 160. [e] Reference 36.

larities, and theoretical results, most particularly as the last relate to a noteworthy configurational problem, the contrasting C_{4v} symmetry observed for Sn_9^{4-} but D_{3h} for the isoelectronic Bi_9^{5+} and the unusual Sn_9^{3-}.

Prior to some general discussion, it is advantageous to also note the related heteroatomic clusters that have been obtained by similar techniques. The use of mixed post-transition elements not only provides some additional configuration examples but also allows the inclusion in clusters of electron poorer elements to the left of group 4 that are missing from homoatomic examples. The results to date are listed in Table III[56-60] and several are shown in Figure 3, namely, $Pb_2Sb_2^{2-}$, $Tl_2Te_2^{2-}$, $TlSn_8^{3-}$, and $TlSn_9^{3-}$. Reactions between solute species and solid alloy appear to be particularly important in the formation and the stability of many of these mixed ions. In several cases, mixed species are obtained when crystals are grown in the absence of alloy, but mainly homoatomic clusters are produced after extended periods in its presence.[41,56-58]

Although one's initial reaction to the prospects of forming mixed-metal species might be that heteroatomic examples would be destabilized by intrinsic differences of the component atoms and the resultant lessening of delocalization, this does not seem to be serious, at least between elements in neighboring groups. In addition, many polyhedral examples have nonequivalent positions whereby heteroatoms presumably can be better accommodated. Even the nominal tetrahedron can be obtained with appreciably different atoms, $Sn_2Bi_2^{2-}$ and $Pb_2Sb_2^{2-}$ evidently representing the first "tetrahedral" ions stable in solution or as normal salts although nominally higher charged examples are known in the condensed solid state in most M^IM^{IV} phases.[62] Although the examples just listed were chosen so that the atoms could be distinguished by X-ray diffraction, the anions in fact are found to be orientationally rather well disordered in the potassium salts. There is little doubt that the other obvious possibilities $Sn_2Sb_2^{2-}$ and $Pb_2Bi_2^{2-}$ also occur and will probably be disordered in such solids. Many more mixed examples can be expected as this approach provides a means to achieve ions of a given electronic configuration with a relatively low charge, for example, those isoelectronic with a variety of polychalcogenide cations.

Recent discoveries indicate that there are also a considerable variety of additional heteropolyatomic anion examples that provide a more-or-less natural bridge between examples of the sort cited in Table III where the bonding is often nonclassical (multicenter) and new varieties of classically bonded and sometimes centered heteroatomic anions. Examples of the latter include solids containing $Sn_2Te_6^{4-}$ (D_{2h}),[63] $SnTe_4^{4-}$ (T_d),[48] and a variety of novel gold and mercury telluride anions such as $Hg_4Te_{12}^{4-}$ and $KAu_9Te_7^{4-}$.[61] There is also NMR evidence for $Te_2X_2^{2-}$ and for the centered ions HgX_2^{2-}, CdX_2^{2-} (linear), TlX_3^{3-}, and SnX_3^{2-} (D_{3h}) where X = Se and Te, all in the presence of crypt.[64] The $HgTe_2^{2-}$ member of the last series has been isolated as the 2,2,2-crypt-K^+ salt.[65]

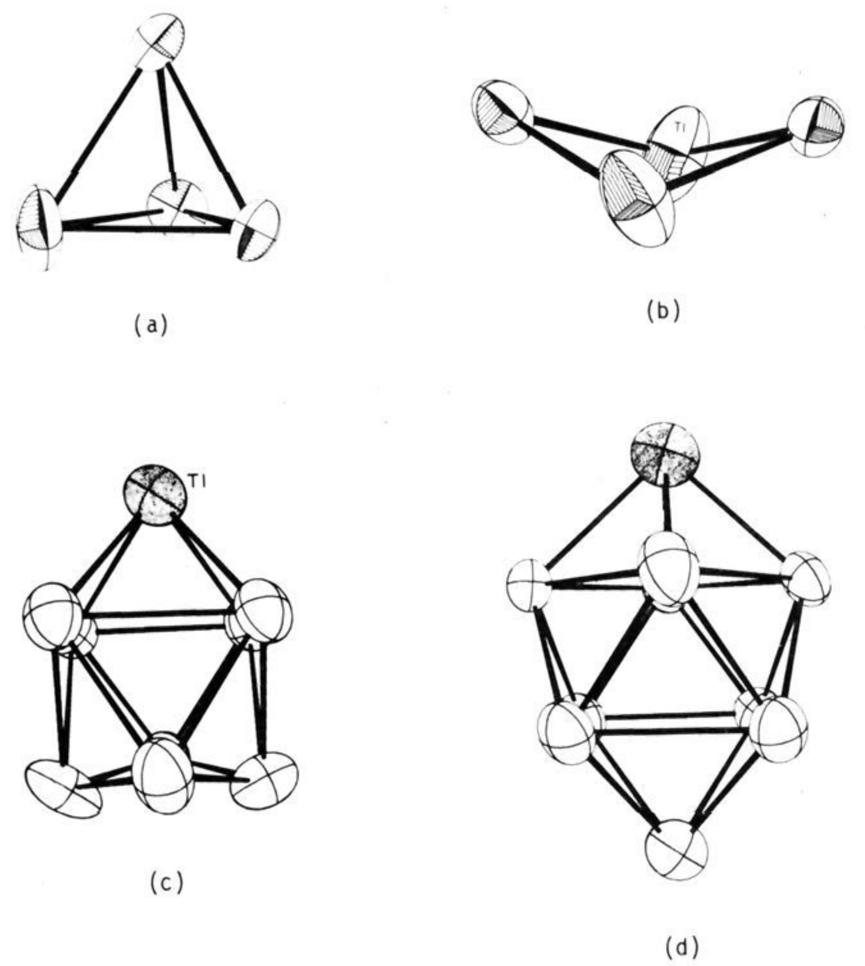


Figure 3. Some heteroatomic Zintl anions: (a) $Pb_2Sb_2^{2-}$ (disordered), (b) $Tl_2Te_2^{2-}$, (c) $TlSn_8^{3-}$, (d) $TlSn_9^{3-}$ (references in Table III).

Members of the previous groups of mixed ions have also been termed "Zintl ions" by some investigators[48,64,66] by the criterion that they were obtained from Zintl phases. The last are polar intermetallic or salt-like phases which were also first generalized by Zintl and which will be described briefly in section IX. This group constitutes a large number of compounds that appear to blend into more conventional polyatomic ions in the limit. For the purposes of this review, Zintl ions considered in detail will be limited to (empty) cluster and related polyhedral species, often with nonclassical bonding, of the character first broadly illuminated by Zintl. Even this border is not clearly defined.

The results of Mössbauer studies on crypt salts of three ions Sn_5^{2-}, Sn_9^{4-}, and $Sn_2Bi_2^{2-}$ that have been structurally characterized as the crypt salts are consistent with the known structures.[66] All isomer shifts are in a range of δ = 2.25–3.00 mm s^{-1} vs. $CaSnO_3$. The asymmetric line obtained at 77 K for the Sn_5^{2-} salt resolves into two components at the extremes of this range. Although these have an intensity ratio of 3.8:1 rather than the expected 1.5:1 for the D_{3h} ion (Figure 2d), the temperature dependence of this ratio is positive and sizable, a change which the authors attribute mainly to the more weakly bound apex atom that gives rise to the smaller component. Very consistent intensity ratios of the order of 1.5–1.8 can be obtained by graphical extrapolation of the data to 0 K. The Sn_9^{4-}

spectrum obtained at 77 K resolves best into a 2.5:1:2.5 population triplet, which was considered to be in good agreement with the expected 4:1:4 relationship, while $Sn_2Bi_2^{2-}$ salt gives the expected single transition and the only example of quadrupolar splitting (1.07 mm s^{-1}). Comparison of the second of these with the reported Mössbauer results for a $Na_4(en)_7Sn_9$[26,27] is not very close, probably because of a somewhat different tin polyhedra, evident Sn–Na interactions (section VIII) and some unavoidable oxidation of the sample in the earlier study.

IV. Stability Principles and Comparisons

Although it is clear that synthetic problems associated with the isolation of many Zintl anions are substantially lessened through the use of the crypt complex for the cation, this may not always be necessary for stability. Isolation of Sn_9^{4-} as well as the probable Sb_7^{3-} and Ge_9^{4-} ions in salts where the sodium cations are more or less sequestered by en has already been noted.[29] Teller et al.[48] have recently obtained both $(Me_4N)_4Sn_9$ (N:Sn = 4:9.4) as a red-brown powder from the rapid reaction of the appropriate potassium alloy with a Me_4N^+ solution in DMF and a well-crystallized $[K(HMPA)_2]_4Sn_9$ by a like reaction using HMPA in en solvent. However, both phases decompose at room temperature, the former to Me_3N and Me_xSn. The use of crypt to gain $HgTe_2^{2-}$[65] as well as Te_3^{2-} probably represents only a convenient route to a large cation and is not a necessity. The same may be true with other anions such as $As_2Se_6^{2-}$ and $Tl_2Te_2^{2-}$.

The postulated effect of cryptation in blocking electron delocalization back onto the cation clearly is altered when the solid decomposition products are more salt-like than metallic, with NaSb and Na_3Sb, for example, and more general questions of phase stability now apply. Other pertinent factors include the well-known advantages of using a large cation with polyatomic anions of limited stability,[68] the improvement in solubility of higher charged ions in solvents with modest dielectric constants such as en that is afforded by larger cations, and simply appreciable changes in solubility patterns. Either the last is fairly significant or the crypt complexation drastically alters the stability of ion pairs judging from the isolation of crypt salts of species such as Sn_5^{2-}, Ge_9^{2-}, and Sb_4^{2-} that have not been evidenced in solution or in solids obtained in the absence of crypt. These advantages for whatever the reasons have led to the apt description of crypt as a "synthetic laxative".[69]

It is noteworthy that the isolated Zintl ions have several isoelectronic analogues among the polyatomic cations investigated earlier, viz., Bi_5^{3+} relative to Pb_5^{2-} and Sn_5^{2-}, Te_4^{2+} compared with Sb_4^{2-} and Bi_4^{2-}, and Bi_9^{5+} vs. Sn_9^{4-} and Ge_9^{4-} (Table II), although distinct differences in configuration between the 22-electron cations and anions in the last group will require subsequent attention.

Notwithstanding, the considerable contrast in the chemical systems used in isolating the polycation vs. the polyanion members is worth noting. Both in effect depend on the nature of the counterion. The tendency for disproportionation into element and normal-valent ions shown by the cations, for example

$$Bi_5^{3+}(X^-)_3 \rightleftarrows BiX_3 + 4Bi$$

can be greatly reduced by the use of a large anion, preferably a nonoxidizing one such as $AlCl_4$, $HfCl_6^{2-}$, etc. Reactions are run either in the molten state at elevated temperatures or in a solvent of very low basicity. This effect can be understood in terms of either the reduced difference in lattice energies of the salts with the two oxidation states or a reduction in the degree of solvation of the more acidic cation in the higher oxidation state. These effects have been viewed as both "acid stabilization"[70] and "anticoordination chemistry".[3]

On the other hand, the disproportionation of the Zintl anions by a reaction like

$$(Na^+)_2Bi_4^{2-} \rightleftarrows 2NaBi + 2Bi$$

is driven by the stability of NaBi and the fixed heat of condensation of the elemental Bi. In this case the idea is to sequester the countercation sufficiently that the decomposition is unfavorable, the metallic NaBi product in the above being replaced by an unknown and probably unstable version $NaL_n^+Bi^-$. Although the initial interpretation of the effect of crypt was one of preventing electron transfer or delocalization back onto the countercation, clearly this role is different when the product is not metallic, for example with NaSb, and we are really back to the effect of an alteration in both cation size and bonding ability on general phase stability.

V. Solution Studies

Nearly all modern information on the solution chemistry of the Zintl ions has come from the NMR studies originated by the late R. W. Rudolph.[71-76] The majority of these were carried out in en without the addition of crypt; although the solution processes are then slower, more concentrated systems are ultimately achieved in many systems.

A convincing proof of the predicted[38] fluxionality of Sn_9^{4-} was supplied by the observation by pulsed Fourier-transform NMR methods of a single ^{119}Sn resonance 1230 ppm upfield from Me_4Sn, this resonance being split by ^{119}Sn–^{117}Sn coupling into the central five lines of the multiplet intensity distribution predicted for a nine-atom cluster. Thus, the three nonequivalent atoms expected on the basis of what is presumed to be the C_{4v} ground-state ion found in the solid are averaged in an *intramolecular* manner on the NMR time scale, possibly via $C_{4v} \rightleftarrows D_{3h}$ interconversion pathway (see below). The tin spectrum is unchanged at −40 °C in liquid NH_3.[71]

The $Sn_xPb_{9-x}^{4-}$ and $Sn_xGe_{9-x}^{4-}$ families of isoelectronic ions were also observed to form with appropriate ternary alloys. Portions of the group of spectra observed for the members of the $Sn_xPb_{9-x}^{4-}$ family by ^{119}Sn NMR and by ^{207}Pb NMR are shown in Figures 4 and 5, respectively. These and the observed Sn–Pb coupling establish that the complete series of nine atom clusters is present. Since the shift appears to be quite regular, the series was taken to be that of the 4− ions throughout. The chemical shift for tin in this series was found to depend linearly on the electronegativity-corrected charge per tin, thus giving an approximate means of predicting the charge per tin on unknown ions (provided paramagnetic and diamagnetic contributions to the shift are relatively invariant). Incidentally, the homogeneous equilibration of Sn_9^{4-} and Pb_9^{4-} ions that

TABLE IV. Zintl Ions Deduced from Solution Studies[a]

ion	study	result	ref
$Sn_xPb_{9-x}^{4-}$	^{119}Sn, ^{207}Pb NMR	all species $0 \le x \le 9$; fluxional	71, 73, 76
$Sn_xGe_{9-x}^{4-}$	Sn NMR	all species $0 \le x \le 9$	72
Sn_4^{2-}	^{119}Sn NMR	single resonance for four atoms, $J = 1217$ Hz	72, 73, 75
	Na:Sn solution analysis by NMR	2:1	75
	effective potential calculations	fluxional via D_{2d} "tetrahedra"	77
Sn_8Sb^{3-}	^{119}Sn NMR	fluxional $Sn_8Sb_x^{n-}$, x assumed, n based on shift and Sn_9^{4-}	71, 76
$TlSn_8^{5-}$	^{119}Sn, ^{205}Tl NMR in en and NH_3	fluxional $TlSn_8$ composition; charge based on Sn_9^{4-} [b]	72
	solution analysis[c]	$Na_5(en)_{1.25}TlSn_8$	76
	^{119}Sn Mössbauer on solid	broad line, ambiguous	66
$Sn_2Bi_2^{2-}$	^{119}Sn NMR, analysis of LiSnBi solution	$Sn_2Bi_2^{2-}$ ($\delta = -1665$, $J = 1606$ Hz)	75, 76
As_4^{2-}	EXAFS on solution of K_3As_5	As_4^{2-} (D_{4h}) + As_6^{4-} (D_{6h}), 50:50	78

[a] In en unless otherwise noted. [b] See text regarding alternate 3− charge assignment. [c] $Na_2Sn_2Tl_3$ alloy composition.

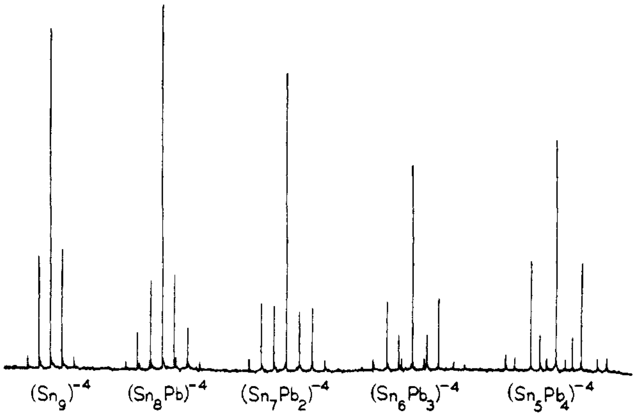


Figure 4. The ^{119}Sn NMR spectrum (increasing H) for the indicated mixture of $Sn_xPb_{9-x}^{4-}$ species in en solution at room temperature (Na^+ cations; $J(^{119}Sn-^{117}Sn) \simeq 260$ Hz; $J(^{119}Sn-^{207}Pb) = 560$ Hz). Reproduced with permission from ref 73. Copyright Plenum Press, 1979.

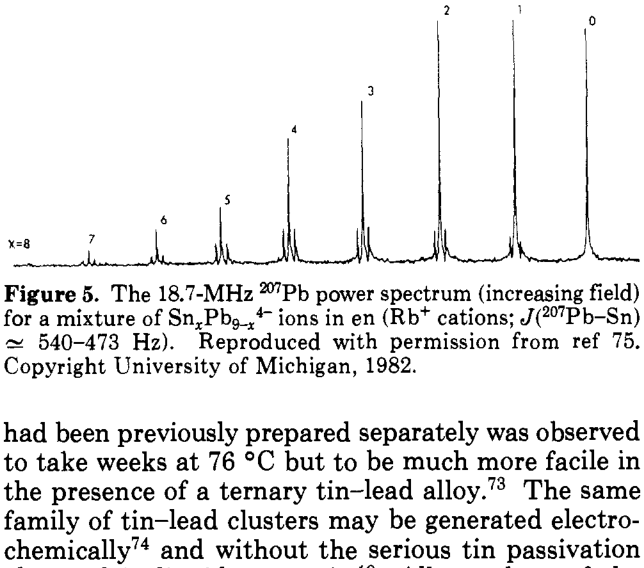


Figure 5. The 18.7-MHz ^{207}Pb power spectrum (increasing field) for a mixture of $Sn_xPb_{9-x}^{4-}$ ions in en (Rb^+ cations; $J(^{207}Pb-Sn) \simeq 540-473$ Hz). Reproduced with permission from ref 75. Copyright University of Michigan, 1982.

had been previously prepared separately was observed to take weeks at 76 °C but to be much more facile in the presence of a ternary tin-lead alloy.[73] The same family of tin-lead clusters may be generated electrochemically[74] and without the serious tin passivation observed in liquid ammonia.[19] All members of the analogous $Sn_xGe_{9-x}^{4-}$ series were also found but without observable Sn-Ge coupling ($I = {}^9/_2$ for ^{73}Ge). The variation in chemical shift with x in this series is distinctly smaller and changes sign.

Changes in the chemical shift of a given species as a function of cation in these solutions clearly manifest the presence of ion pairing.[75,76] For example, the ^{119}Sn shifts (vs. Me_4Sn) for Sn_9^{4-} in en vary rather smoothly from −1115 ppm for Cs^+ to −1241 ppm with Li^+ and −1253 ppm with 2,2,2-crypt-Na^+, the larger crypt or the well-solvated lithium being similar in effect. The comparable range for the ^{207}Pb shift in Pb_9^{4-} with alkali metal is −891 to −1224 ppm.

Table IV lists the above together with other ions for which some appreciable evidence has been obtained from solution studies, mainly NMR. One of the more remarkable is the result of equilibration of alloys in the $NaSn_{1-2}$ range with en.[72] The dilute, yellow-red solution contains a high yield of a species with a single ^{119}Sn resonance (δ −1895) split by ^{117}Sn coupling ($J = 1224$ Hz) in a manner clearly appropriate to a four-atom cluster. These data suggest either a tetrahedron or a lower symmetry fluxional species, the former being the more reasonable for such a large J value. A rough NMR analysis using internal ^{23}Na and ^{119}Sn standards together with the shift-per-charge on tin are consistent with an 18-electron Sn_4^{2-} species. Of course, a normal tetrahedral unit would be expected to be paramagnetic and Jahn–Teller unstable. On the other hand, fluxionality of a diamagnetic species about a tetrahedral average is supported by effective potential calculations for Sn_4^{2-}, dynamic second-order Jahn–Teller distortion producing a fluxional diamagnetic system that circulates via pseudorotation among the six D_{2d} configurations, i.e., elongated and compressed tetrahedra.[77] The calculated barrier is 40 kJ mol^{-1}. Observation of the limiting spectrum of the rigid ion at lower temperatures would certainly be valuable. Some evidence for a similar ion for germanium has been obtained from an X-ray study of what was apparently $(2,2,2\text{-crypt-}Na^+)_2Ge_4^{2-}$. Although a tetrahedral-like anion seemed evident (d(Ge–Ge) ≈ 2.78 Å, $B \approx 11$ Å^2), the anion was partially disordered about an effective inversion center, and the structural solution was not really completely satisfactory ($R = 17.0\%$).[47] (The preliminary report of a crystalline salt of Sn_4^{2-}[79] was in error.[56])

A spectrum attributed to a fluxional $TlSn_8^{5-}$ was obtained from M_2Sn_2Tl alloys (M = K, Na) in both en and NH_3, the composition being uniquely established via Sn–Sn and Sn–Tl coupling. The 5− charge was based on a total solute analysis $Na_5Sn_{8.4}Tl\cdot1.25en$ for the residue isolated by evaporation of en. The charge assignment is of course at variance with the one isolated example, $TlSn_8^{3-}$ (Table III); the latter also involves heteroatom substitution at a lower order vertex contrary to prediction for the electron-poorer thallium in the 5− ion.[72] The low en content of this solid obtained presumably allows sizable Na–Sn interactions, and these lead to the rather broad and uninformative ^{119}Sn Mössbauer spectrum obtained for this material.[66]

Equilibration of a variety of Na–Sn–Sb compositions with en gives rise to a new species that contains eight tin atoms and is also fluxional according to tin NMR ($J = 81$ Hz)[76] (an earlier analysis assigned this to nine atoms[71]). No Sn–Sb coupling was seen, presumably because all antimony isotopes are quadrupolar. Although the antimony content could not be determined, a reasonable Sn_8Sb^{3-} ion isoelectronic with Sn_9^{4-} was suggested. However, the ^{119}Sn shifts found for Sn_8Tl^{5-} and Sn_8Sb^{3-}, 61 and 108 ppm downfield from (less negative than) Sn_9^{4-} for the sodium salts, would certainly be more consistent with expected electronegativity equalization effects and the shift per charge trends found for the $Sn_xPb_{9-x}^{4-}$ series (see Figure 4 in ref 80) if the former were instead Sn_8Tl^{3-}, the same as known structurally. A plausible fluxionality in this event is not clear; see section VII.

Other ions have been postulated on the basis of similar or less NMR evidence, Sn_8Bi^{3-} (mixed with $Sn_2Bi_2^{2-}$), for example.[75,76] There are also some fascinating but incompletely characterized species obtained by reactions of Sn_9^{4-}, Pb_9^{4-}, or $TlSn_8^{5-}$ with $Pt(PPh_3)_4$ or $Pd(PPh_3)_4$ in en.[81,82] The first pair of reactants give the best characterized product $(PPh_3)_2PtSn_9^{4-}$, the charge being assumed, while Pb_9^{4-} forms a seemingly analogous species. The reaction of $TlSn_8^{5-}$ was thought to give $(PPh_3)_2MTlSn_8^{5-}$, M = Pt, Pd, or similar species; although the 2, 5, and 8 numbers in this formulation were in effect assumed, the ^{119}Sn chemical shifts are very similar to those of the dinuclear products above. The thallium-containing species subsequently exchanges with tin, evidently at the surface of the alloy, to form the previously known $(PPh_3)_2MSn_9^{4-}$ ions. The species are evidently not very stable at room temperature. Additional supporting evidence is needed but the prospects of an interesting chemistry are manifest.

The one EXAFS study indicating the existence of As_4^{2-} analogous to its antimony and bismuth brethren that have been characterized in the solid state will hopefully be followed by other studies of this character, for example, on the polybismuth solutions which, based on color changes, should contain more than just the isolated Bi_4^{2-} ion ($Bi_6^{2-} \triangleq Te_6^{4+}$?). This means of analysis will naturally be facilitated if auxiliary information about solution composition and the number of species present is available.

Some novel applications of Zintl ion solutions should be noted. Oxidizing polymers such as a polyimide can be topochemically metallized by reaction with such solutions, the alkali-metal cations intercalating as the anion reduces the polymer to anion centers while thin films of the oxidized (neutral) metal from the anion are simultaneously deposited on the surface.[83] Solutions of K_4Sn_9 in en reduce graphite, $HfTe_2$ and the like, the potassium being intercalated while tin metal deposits only on edges of the layered substrate.[84]

VI. Configuration, Bonding, and Electronic Considerations

The so-called "naked" clusters formed by the post-transition elements are in most respects not something apart in configuration and bonding. As is usually the case, certain bonding arrangements are favored and occur in diverse compounds, and a close similarity in skeletal electron count and bonding between these clusters and the boranes, $B_nH_n^{2-}$ particularly, has been recognized for some time.[36] Thus, there is little that is very unusual about the configurations found for most of the Zintl ions, particularly for the more electron-poor and clustered group of these, although some provide new examples of predicted configurations. The polyhedral shape–electron count relationships generally fall into the well-known categories described by Wade's rules,[85,86] namely, the deltahedral or closo type with *n* atoms bonded by 2*n* + 2 electrons (Ge_9^{2-}, Sn_9Tl^{3-}, Pb_5^{2-}), the nido species with 2*n* + 4 skeletal electrons where one vertex has been removed from the closo configurations for *n* + 1 atoms (Sn_9^{4-}), and the arachno members with still one fewer vertex and 2*n* + 6 electrons (Sb_4^{2-}, Bi_8^{2+}). The long standing exception to these regularities has been the closo but 2*n* + 4 ion Bi_9^{5+} (tricapped trigonal prism), the explanation of which will be considered shortly. (The tetrahedral cluster limit also requires a little fancy footwork—in the above terms the well-behaved tetrahedral species with 2*n* + 4 electrons exemplified here by $Sn_2Bi_2^{2-}$ is viewed as the nido product of a trigonal bipyramid; the proper 2*n* + 2 closo tetrahedron would be paramagnetic and Jahn–Teller unstable, but, interestingly, such a diamagnetic species Sn_4^{2-} has been proposed to be fluxional about the ideal configuration.)

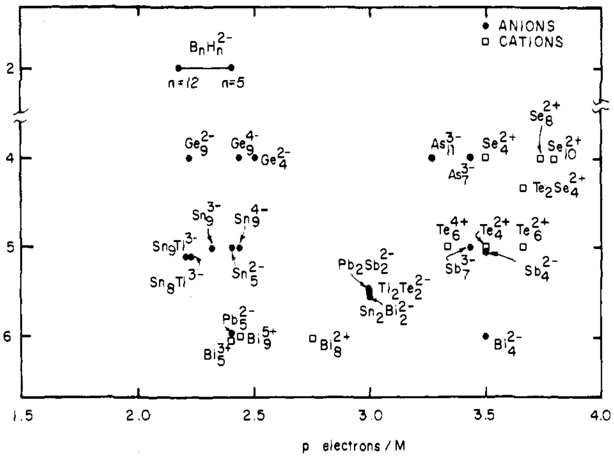


Figure 6. The p-electron count per cluster atom for known anions (●) and some cations (□).

The distribution of species in terms of p electron count per cluster atom for the structurally characterized Zintl anions, some cations, and the polyboranes are shown in Figure 6 as a function of period. The 2*n* + 2 lower limit is clearly seen at ~2.25 skeletal electrons per atom (2 + 2/*n* more precisely). Incorporation of very many group II or III elements into these ions presumably must be accompanied by enough of an electron richer element to achieve this minimum. (The obviously special type of metal–metal bonding shown by mercury is a notable exception.) At the other extreme, valence electrons in the mainly cationic clusters with more than about three electrons per cluster (2*n* + 6 is closer) can be partitioned into ~2.2–3 skeletal bonding electrons with the remainder appearing as the nonbonding lone pairs that are so important in determining the shape of the molecule or ion.[58] The latter occur in an even higher proportion in the unlisted polychalcogenide anions with more than four p electrons per atom.

It is worth noting that in spite of the relatively low coordination numbers and electron counts in these Zintl anions, they do not act electron deficient in the sense of being strongly electrophilic or acidic; in fact, the only evident interaction of en with the anions in all the solids studied is the apparent hydrogen bonding of en to Te_3^{2-}. In contrast, Te_4^{2+} and Se_4^{2+} clearly interact with such poor bases as SbF_6^-, $AlCl_4^-$, and $Al_2Cl_7^-$ in their solid compounds.[8,42] Orbital-wise, the relatively negative open face of Sn_9^{4-} is quite analogous to the products obtained either by vertex elimination from deltahedral $B_nH_n^{2-}$ or the related carboranes $C_2B_{n-2}H_n$ or by their reductive polyhedral expansion except that the open face is closed and stabilized by cobalt, iron, etc. atoms in the latter in carbollide-type complexes.[87,88] The tin cluster is obviously stable without such a feature, but the possibility of analogous reaction of the open face is still intriguing and unexplored.

Only a few of the clusters previously described are amenable to classical, two-center bonding descriptions. Qualitative multicenter schemes can be applied to Pb_5^{2-} and Bi_9^{5+}, viz., eight three-center and three four-center bonds in the latter.[89] But for the most part, only molecular orbital approaches have provided general and energetically useful descriptions. Some of the distinctive closed-shell or saturated bonding characteristics of these Zintl clusters and the analogous cations can be understood in these terms as originating with the relatively small, atomic orbital basis set involved. This is in most cases effectively p orbital only with MO's derived from valence s being effectively core states, a factor that was first recognized in the analogous polybismuth cations.[36,90] Obviously, such a circumstance makes approximate molecular orbital calculations both easier and more creditable although the intrusion of important relativistic effects with the heavier elements may "even the score". In fact, an apparently meaningful factor that is not evident in conventional extended Hückel calculations is the significantly diminished binding energy per atom calculated for a variety of anionic clusters of sixth period elements, lead, for example, that is found on inclusion of spin-orbit coupling. This predicts a binding energy for polylead ions only about 60% of that calculated for the analogous tin species, with those for bismuth and germanium intermediate.[91] These binding energies are naturally only part of the story in a cyclic description of decomposition reactions; in fact, another term, the heats of atomization of the individual elements, somewhat parallels the calculated cluster binding energies, a rather sensible result in itself.

By and large, the published collection of calculated molecular orbital energy results agree fairly well with observation as far as ground-state configurations.[34,40,91,92] But a significant problem in this sort of prediction is the choice of dimensions of unknown configurations that perhaps are only slightly higher in energy. This will be evident in the following consideration of some characteristics of nine-atom species.

VII. Problems with Nine-Atom Polyhedra

Two features of the 22-electron cluster examples have stirred considerable interest: their fluxionality and the contrasting configurations of C_{4v} for Sn_9^{4-} and D_{3h} for the rule-breaking Bi_9^{5+}. On the other hand, the 20-electron polyhedra typified by Ge_9^{2-} and $TlSn_8^{3-}$ are properly closo (D_{3h}) or approximately so, and low-energy alternatives are not known to exist. Some helpful clarifications regarding important factors in the configurational dilemma for 22-electron, nine-atom polyhedra are provided by a combination of the recent isolation of the intermediate Sn_9^{3-}, which is also D_{3h}, dimensional comparisons among the D_{3h} polyhedra, and some EHMO calculational results.

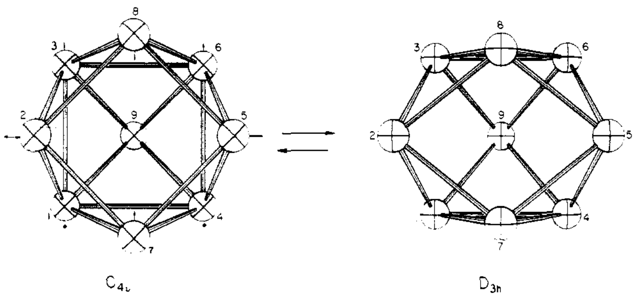


Figure 7. Nine-atom polyhedra: an interconversion pathway between the unicapped antiprismatic (C_{4v}—left) and tricapped trigonal prismatic (D_{3h}—right) examples.

The configurational assignment of many nine-atom polyhedra must be decided with some care since the two most common limits, the unicapped archimedean antiprism (C_{4v}) and the tricapped trigonal prism (D_{3h}), are not very far apart in either distances or angles; in fact, they can be easily confused or misjudged if they are classified solely by inspection of drawings made from selected perspectives. The bases for their differentiation can be found in Figure 7 which also illustrates the probable pathway[93] for a $C_{4v} \rightleftarrows D_{3h}$ interconversion between these two through a C_{2v} intermediate and along a suitable extended vibration of each species.[92] The left view is along the fourfold axis of the C_{4v} model with the square base toward the reader. Generation of a D_{3h} polyhedron with the threefold axis vertical can be accompanied by the indicated motions, compression of the front square along the edge 7–8 with (usually) an elongation of the 1–3 and 4–6 edges of the capped square to generate a trigonal prism. Obviously, an equivalent pathway is a generation of an alternate trigonal prism 3–6, 2–5, and 1–4 with a horizontal threefold axis, which process when cycled completes the scrambling of the atoms. The more discriminating distances are the diagonals in each of the two squares in the C_{4v} limit, the three edges that describe the height of the trigonal prism, and the separations of the capping atoms 2, 5, and 9 in the latter. More definitive, however, are the dihedral angles,[93] particularly when clusters of different elements are involved. The more useful angles are those defining the planarity of the square base in C_{4v} (2–7–8 vs. 5–7–8, $\delta = 0°$, is one set) and one of the two pair between opposed faces around the waist, e.g., 3–6–8 and 1–4–7, that become the basal members of the trigonal prism ($\delta = 180°$). An important parameter for the D_{3h} polyhedron is also the height-to-basal edge ratio (h/e) of the prism, i.e., $d(1–3)/d(1–4)$.

The dihedral angles for the nine-atom Zintl ions and Bi_9^{5+} are sorted out in Table V; the most informative values described above are listed in the first two columns. The good approximation of Sn_9^{3-} as D_{3h} is clear from the first column (and the prism heights therein differ by only 0.045 (3) Å) while its difference from Bi_9^{5+} in the narrow group of adjoining vicinal angles depends on h/e for the prism; $TlSn_8^{3-}$ is certainly similar. At the other extreme, Sn_9^{4-} (and KSn_9^{3-}—later) is close to C_{4v}, and the best trigonal prism heights differ by more than 0.9 Å. The two germanium polyhedra are distorted from the end members; Ge_9^{4-} is clearly derived

Table V. Some Dihedral Angles (δ, deg) in Nine-Atom Polyhedra[a]

D_{3h}-type faces (Figure 6)		trigonal prism (opposed) 1-4-7, 3-6-8	cap to cap (vicinal) 2-7-8, 5-7-8						prism end to cap (vicinal) 3-6-8, 2-3-8						
D_{3h}	Bi_9^{5+}	180		22 (× 3)[b]								43 (× 6)[b]			
D_{3h}	Sn_9^{3-}	179	17	18		18			40		40	41	41	41	42
D_{3h}[c]	$TlSn_8^{3-}$	177	16	(17)[d]		(19)[d]			(35)[d]		(36)[d]	41	41	42	42
C_{2v}	Ge_9^{2-}	171	8	25		23			38		36	44	47	45	45
~C_{4v}	Ge_9^{4-}	162, 156	5		32		24	32		33		51	54	53	51
C_{4v}	Sn_9^{4-}	158, 158	3		30		29	29		32		52	53	54	55
C_{4v}-type faces		waist, opposed	base	cap to waist, vicinal								waist to waist, vicinal			

[a] Structural references in Tables II and III. [b] Dependent on h/e of the prism (see text). [c] Ignoring thallium atom. [d] Defining plane contains the thallium atom, which effectively reduces δ relative to that for homoatomic species.

from C_{4v} (the prism heights differ by 0.6 Å) while Ge_9^{2-} though seemingly derived from D_{3h} is (inexplicably) distorted 25–30% toward C_{4v}, one prism height now being 0.33 Å longer than the other two (Figure 2c). (This does not appear to be along a suitable fluxional pathway for 20-electron D_{3h} species.) There is an also older structure of Bi_9^{5+}, the original $Bi_{12}Cl_{14}$,[94] in which the cation is ~25% of the way along the same path. Crystal packing was originally invoked to "explain" this, but it is now more plausible as this distortion is probably along a low barrier or "soft" pathway.

In this connection, it should be mentioned that the tin polyhedron resolved in $Na_5(en_9)_7Sn_9$ is distorted in virtually the opposite direction, with *two* edges of what would be the best trigonal prism 0.6 Å *longer* than the third.[29] But in this case strong interactions of tin atoms on each of the long edges with Na^+ seems responsible, as will be described in the next section.

Calculations on the stability of different configurations for 22-electron species relevant to possible fluxionality have been carried out several times and by varying means. Two additional problems with such deductions are probably as important as the method. First, a sizable dipole for the C_{4v} alternative disappears on conversion to the D_{3h} model, a factor which should bias the results in favor of the former in the usual polar molecular solvents. In contrast, Bi_9^{5+} can be observed only under acidic conditions with nonpolar anions or, in principle, also in nonbasic solvents. Second is the uncertainty regarding the proportions of unknown polyhedra, particularly the D_{3h} version of the nine-atom Zintl anions. Scaling with simple proportions is not very realistic. It is now known that the principal difference among various members is in the relative height-to-edge ratio (h/e) of the trigonal prism, that in Bi_9^{5+} being 10–15% greater than that in Ge_9^{2-}, $TlSn_8^{3-}$, and $Bi_9H_9^{2-}$,[35] with Sn_9^{3-} intermediate. This actually involves opposite changes in both the height and the basal edge, appropriate to the orbital occupied (below), and these differences can have a significant effect on the calculational results.

Some CNDO and EHMO calculations using C_{4v} and D_{3h} models that include all of these dimensional subtleties provide the energies given in Table VI.[34,47] (Those for observed configurations are given in boldface type.) The energies calculated for the observed configurations of these ions differs from those of the ideal limit only for Ge_9^{2-} (−0.04 eV). The CNDO predictions of configuration for M_9^{4-} species are seen to favor the D_{3h} limit slightly, contrary to the known structures, and in fact the original fluxionality predictions by this method certainly benefited from some luck in the choice of dimensional parameters. The EHMO results seem more credible in this respect, and the importance of the prismatic dimensions in D_{3h} is evident (h/e is given in parentheses). The $C_{4v} \rightleftarrows D_{3h}$ interconversion clearly involves the smallest energy difference (and virtually no barrier) for the 22-electron species, as is observed by NMR for Ge_9^{4-}, Sn_9^{4-}, and Pb_9^{4-} and implied by these data for Bi_9^{5+}. Calculations for the unknown species Sn_9^{2-} (D_{3h}) give some evidence for its limited stability. The orbital energy sum in this instance is greatest for a 1.01 h/e ratio, decreasing by 0.7 eV at h/e = 1.15. The a_2'' LUMO for Sn_9^{2-} is rather isolated, lying within what would otherwise be a gap of 6.2 eV and only 1.6 eV above the e′ HOMO. (The same is true for the known $B_9H_9^{2-}$.[35]) This a_2'' orbital becomes the HOMO in Sn_9^{3-} and Sn_9^{4-} (D_{3h}), and in the process its energy approaches that of the other occupied MO's. A C_{4v} configuration for Sn_9^{3-} is out of the question as it would require an e^3 HOMO; the total energy also appears to be significantly less.

According the the orbital energy data, the elongation of the Bi_9^{5+} ion along the threefold axis (with a simultaneous reduction of the length of the basal edge

TABLE VI. Energies (eV) from Molecular Orbital Calculations on C_{4v} and D_{3h} Configurations for Known Nine-Atom Polyhedra[a]

	C_{4v}	D_{3h}, h/e[b]
	CNDO–SCF Atomization Energies	
Ge_9^{2-}	54.88	**55.99** (1.10)
		56.62 (1.06)
Ge_9^{4-}	**44.54**	44.49 (1.10)
		45.85 (1.15[c])
Sn_9^{4-}	**28.61**	29.10 (1.15[c])
		28.94 (1.01[c])
	Extended Hückel (iterative) Orbital Energies	
Sn_9^{4-}	**-311.8**	-310.8 (1.15[c])
		-309.9 (1.01[c])
Sn_9^{3-}	-336.9[d]	**-338.5** (1.08)
		-338.2 (1.01)
Bi_9^{5+}	-740.0	**-740.1** (1.15)
		-739.2 (1.08)

[a] Energies for observed configurations in bold face type. [b] Height to basal edge lengths in trigonal prism. [c] Basal edge decreased 0.12 Å. [d] Only one cycle.

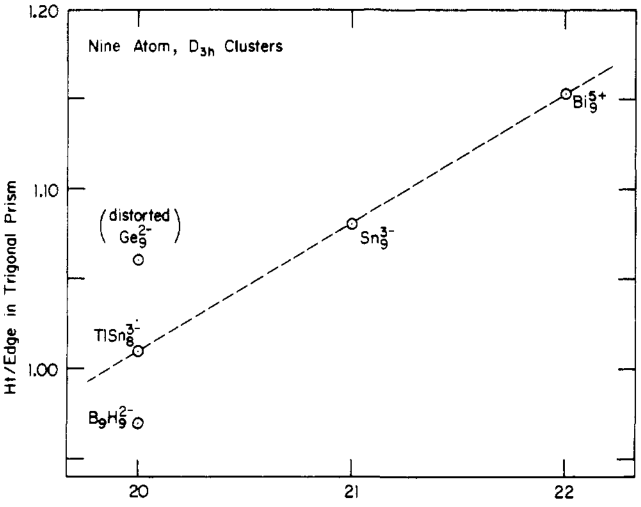
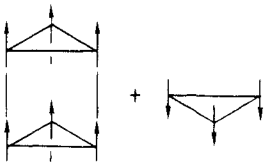


Figure 8. The dependence on skeletal electron count of the height-to-basal-edge ratio in the trigonal prism of known nine-atom, D_{3h} polyhedra.

of the prism, below) clearly represents an alternative to the "correct" C_{4v} structure and experimentally is found at least in media where the dipole moment of the latter would be of no benefit. Some of the driving force for the formation of the 22-electron Bi_9^{5+} derives from the reduction of the relatively high 7+ charge of the normal closo ion, a process that is disfavored for Sn_9^{4-}. That this elongation is a reasonable and feasible distortion with 22 electrons was evidently first stated in graph theory terms by King.[95] It was later observed[47,96] that the a_2'' HOMO is σ-antibonding with respect to the height of the trigonal prism, π-bonding as far as the basal edges thereof, and weakly bonding for the waist or capping atoms. The first two effects can be easily seen in the character of the symmetry orbitals in 2 that, with different coefficients, go to make up this MO. Accordingly, the principal dimensional changes that occur on occupation of this a_2'' MO are not just an increase in the prism height but also a decrease in the basal edge and perhaps a tighter bonding of the capping atom. The second is clearly seen with $TlSn_8^{3-}$ (face-capping Tl) relative to Sn_9^{3-} where the basal edge decreases from 3.12 to 3.06 Å while the capping distance (omitting Tl and two partially disordered Sn atoms in the former ion) shows only a marginal decrease from 2.96 to 2.94 Å.



2

The demonstrated effect of the addition of two electrons to the $2a_2''$ level of the nine-atom, D_{3h} polyhedron is shown in Figure 8 as the observed height-to-edge ratio (h/e) as a function of the skeletal electron count.[39,97] As is seen, Sn_9^{3-}, $(2a_2'')^1$, is beautifully intermediate between $TlSn_9^{3-}$ and Bi_9^{5+} where $2a_2''$ is empty and doubly occupied, respectively. (One long prism edge each in $TlSn_9^{3-}$ and Ge_9^{2-} was omitted in the calculation of h/e, this divergence in the former case doubtlessly arising from coupling of atoms in the refinement; otherwise the h/e values would be 1.03 and 1.10, respectively.)

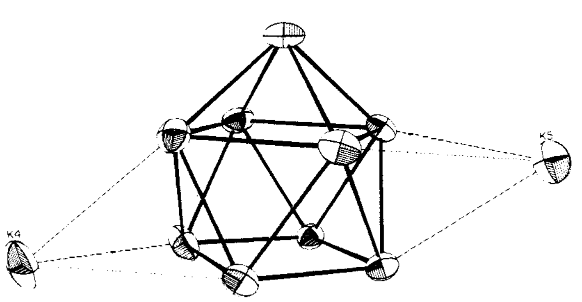


Figure 9. The repeat unit in the infinite anion chains in $(2,2,2\text{-crypt-K}^+)_3(KSn_9^{3-})$. The potassium atoms lie at inversion centers.[101]

The possible fluxionality of 20-electron D_{3h} ions such as Ge_9^{2-} and Sn_9^{2-} is not so easy to assess. The C_{4v} end member in the pathway shown in Figure 6 is not feasible now because of its $(e')^2$ HOMO, but other mechanisms have been suggested.[93] In addition, this exclusion will not apply to $TlSn_9^{3-}$ *if* thallium is not in the capping position on the fourfold axis. The $B_9H_9^{2-}$ ion is not fluxional by NMR,[98] although *s* mixing is clearly greater here and a more rigid species would be expected. Nonfluxional Zintl ions on the NMR time scale appear to be very rare.[75]

VIII. Cation–Cluster Interactions

The effects of ion pairing for Zintl ions in en are implicit in the NMR data, but significant interactions of this sort in most of the solid phases studied are precluded by the presence of cryptated cations. A few contrary examples do suggest that some novel structural effects remain to be discovered. Of course, these examples really just represent bridges to the type of interactions found in the solid state in Zintl phases (section IX).

Salts of two relatively stable anions obtained from en solution are known to show intimate ion association. In $Rb_3As_7{\cdot}3en$ the rubidium atoms bridge between the two-coordinate atoms of the nominal As_7^{3-} ion (C_{3v}), these being coordinated by en only on the outside of the Rb_3As_7 complex. A similar arrangement is found in $Na_4P_{14}{\cdot}6en$. Such complexes are thought to be important in the fluxionality of P_7^{3-} (by NMR) in THF and en.[99]

A remarkable example of a not-so-naked tin cluster was evidently the result of a reaction between KHgSn and an accidental deficiency of crypt in en, which yielded $(2,2,2\text{-crypt-K}^+)_3(KSn_9^{3-})$.[100,101] The KSn_9^{3-} unit in this consists of an infinite chain of alternating, nominal K^+ and Sn_9^{4-} units as shown in Figure 9. The nonequivalent potassium atoms lie at centers of symmetry and are quite free of coordinated en, being surrounded by the crypt cations and six tin atoms in two clusters, four at 3.55–3.76 Å and two more at 4.11 or 4.22 Å in a distorted antiprism. The average K–Sn distance in the first group is close to the minimum value observed about six- or eight-coordinate potassium in K_4Sn_4.

Distances in the tin cluster show remarkably little evidence of the neighboring potassium relative to those in the isolated anion in $(2,2,2\text{-crypt-Na}^+)_4(Sn_9^{4-})$ (Figure 2a). The Sn–Sn distances in KSn_9^{3-} in detail average slightly longer (0.016 Å) when both atoms have potassium neighbors than for other distances of the same kind. The cluster is also slightly distorted angularly,

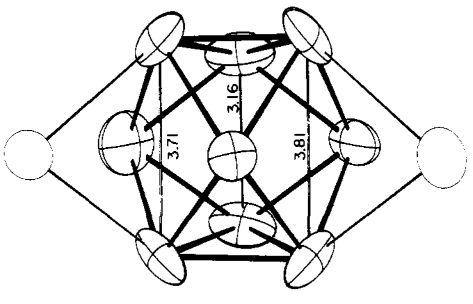


Figure 10. The $Na_2Sn_9^{2-}$ unit in $Na_4(en)_7Sn_9$ with crossed (30%) ellipsoids for tin.[29]

the two nominal squares in the C_{4v} polyhedron being slightly elongated toward the potassium atoms along the diagonals; the first three dihedral angles in the Table V format are still close, 156°, 160° and 1°. It is certainly not clear that this arrangement represents more than an electrostatic interaction. The C_{4v} anion is not expected to be particularly deformable along this direction, which is not along the fluxional route of Figure 7 since the Sn_3 triangles coordinated by potassium involve two atoms on the bottom square.

A quite different result of the interaction of a cation with Sn_9^{4-} appears in the lower symmetry polyhedron present in $Na_4(en)_7Sn_9$.[29] The view shown in Figure 10 is approximately a vertical trigonal prism that is clearly distorted away from the fluxional pathway discussed before with two edges elongated by over half an Ångstrom from a slightly short value for the third ($h/e \approx 1.06$). The source of the distortion is evidently two sodium atoms (open ellipsoids) that are three rather than four coordinate to nitrogen in en and bridge the long edges of the prism. This can also be viewed as the result of capping two of the folded rhomboidal side faces of the tricapped trigonal prism, distorting both of these toward square planar although the diagonals of these still differ by ~0.6 Å. The (rather large) thermal ellipsoids do not suggest that the resolved figure is actually the result of superposition of two capped antiprismatic polyhedra.

The observed Na–Sn distances, 3.49–3.59 Å ($\sigma = 0.02$ Å), are relatively about 0.2 Å longer than those found in KSn_9^{3-}, Figure 9, when the difference in cation radii is taken into account. The magnitude of the effect with sodium suggests the barrier to this distortion of the cluster is much smaller than that in KSn_9^{3-}.

IX. Zintl Phases—New Opportunities

Obviously, many Zintl ion species remain to be detected and characterized both in solution and as solid salts. But the next frontier in this area may be the variety of unusual clusters or aggregates of the main-group elements that are found in the so-called Zintl phases, particularly those that cannot be readily interpreted by classical valence rules.

The term "Zintl phase" was first applied by Laves[20] to the binary compounds formed between the alkali or alkaline-earth elements and the main-group elements from group 4 on—that is, to the right of the "Zintl boundary". (Use of the term *post-transition* rather than *main group* is also appropriate save for a few pertinent compounds of aluminum and silicon.) These combinations not only yield some Zintl anions in solution but also produce many rather polar or salt-like phases. The most reduced member for each is usually a classical valence compound in which the more noble member achieves a filled octet and an $8 - N$ oxidation state in salt-like structure, for example, Na_3As, Mg_2Sn, and Mg_3Sb_2 which occur in LaF_3, CaF_2, and La_2O_3 antitype structures, respectively. An important intermetallic structure type discovered by Zintl was that of NaTl where the thallium sublattice occurs in the diamond structure (and the sodium likewise).[18] This obviously can be interpreted as an isoelectronic Tl^- array in the limit of complete charge transfer.[102]

Subsequent applications of the term "Zintl phase" have generally been based on the structural characteristics of such polar phases. An expanded definition by Klemm and Busmann[103] encompassed many more phases by including those in which the anion lattices have structures and electron counts of neighboring elements. Examples of the latter[62] are $CaSi_2$ (arsenic-like layers of Si), KGe, $BaSi_2$, and Na_2Tl (tetrahedra isoelectronic with P_4 and As_4), $CaGa_2$ and $CaIn_2$ (graphite and distorted diamond lattices, respectively), $SrSi_2$ (a three-dimensional lattice of three-coordinate Si), and NaSb and CaSi (helical and zig-zag planar chains, respectively, analogous to gray selenium). This way of looking at electronic requirements is generally familiar to chemists, based as it is on conventional octet ideas, and can be generalized to cover many filled-band examples of AB semiconductors with diverse A–A, B–B, or no homoatomic bonding.[104] Naturally the extreme charge asymmetries implied by the oxidation state assignments do *not* represent real charge distributions.

A more recent and broader definition includes any heteropolar phases in which classical two-center valence rules satisfactorily describe the bonding of the post-transition elements in the "anions".[62] It is clear that this encompasses a large and diverse group including not only such members as CaP (Na_2O_2-type), Ba_5Pb_3 (equal numbers of isolated atoms and dimers), and Sr_3As_4 (As_4^{6-} chains) but also analogues of sulfate, phosphates, silicates such as $Ba_4(GeAs_4)$, and their condensation products, some of which naturally represent new types of connectivities.[62,105,106] The conventional bonding in many of the last category has led this author to resist a recent tendency[48,66] to broaden the definition of Zintl ions to include anything obtained in or isolated from a solution of a Zintl phase.

As first noted by Zintl,[20,102] substantially all of the classical Zintl phases exhibit properties reflecting the heteropolar bonding and their dissimilarity from typical alloys: brittleness, color, relatively fixed stoichiometry, and substantial heats of formation and negative volume changes relative to the elements. All are probably semiconductors (or semimetals) although this has not been ascertained in most cases. However, it is clearly incorrect to consider the heteroatomic (cation–anion) interactions in these as ionic anymore than CuSe or PbI_2 is "ionic". The use of the convenient cation and anion terms should not imply this either. An important covalency between these "ions" seems to be particularly evident in some of the extremes found within Zintl phases containing lithium.

Probably more interesting and more related to nonclassical Zintl ions are the polar phases in which aggregates formed by the more electronegative elements do not readily succumb to straightforward two-center bonding interpretations with conventional oxidation state assignments. In principle these may result when excess electrons make the phase metallic (AlB_2), when a significant participation of the electropositive element in the anion bonding scheme generates less intelligible bonding interactions, or when unprecedented clusters are found.

Two classes of compounds that show persistent and unusual aggregation of the post-transition elements even in binary phases involve either lithium or gallium or both. In the former case one finds, for instance, dimers of the heavy elements in Li_5Sn_2 and Li_9Ge_4, dimers and isolated atoms in Li_8Pb_3, Li_7Sn_2, $Li_{13}Si_4$, and Li_2Sb, bent trimers in Li_7Sn_3, zig-zag chains in Li_9Al_4 and Li_2Ga, pentagons plus isolated atoms in $Li_{11}Ge_6$, and puckered layers in Li_3Al_2 and LiSn.[105] Such inexplicable bonding arrangements between the heavy elements boggle the mind!

As an example of the progress that can be made, some understanding is now available relative to bonding in the remarkable $Li_{12}Si_7$ which contains planar Si_5 rings and trigonal-planar Si_4 stars. The compound is semiconducting and diamagnetic, indicating a filled band with an unconventional bonding behavior.[107] A theoretical study shows that covalent Li–Si bonding is important, especially with the Si_4 star where sets of lithium distributed around it effectively lower the energies of the σ^* and π^* levels to allow their occupation.[108] Similar studies of Li_8MgSi_6 where there are five-membered rings and isolated silicon atoms show that a more normal assignment is reasonable (if a cyclopentadienide-like Si_5^{6-} limit is normal).[109]

The variety of structures that may be provided by nature when one goes exploring is well illustrated by the remarkable group of polyhedral gallium clusters found in gallium-rich binary phases formed with the alkali metals. Compositions like K_3Ga_{13},[110] $RbGa_3$,[111] and Na_7Ga_{13}[112] exhibit complex structures containing large, interconnected, and usually empty gallium polyhedra: icosahedra, dodecahedra, octadecahedra, etc. reminiscent of boron chemistry.[113] Electron transfer from the alkali metal to the gallium network seems evident. The majority of the arrangements may be interpreted as Zintl phases fairly well with the aid of Wade-like rules of the sort derived from boron polyhedra.[106,113] Lithium examples again present difficulties. Electrical properties have evidently not been measured to confirm that the phases are semiconductors. The more condensed clathrate-like structures such $M^I_8M'_{46}$, M′ = Si, Ge, and Sn,[104] as well as the remarkable infinite-bonded Li_7Ge_{12}[114] do not appear appropriate for the present consideration.

Finally, it is appropriate to note that few isolated intermetallic phases do appear to contain relatives of the square planar Bi_4^{2-} Zintl anion. The compound $Ca_{11}Bi_{10}$ contains Bi_4 groups (D_{4h} point symmetry), Bi_2 dimers, and isolated bismuth atoms in a ratio of 1:4:8, and the Ca–Sb, Yb–Sb, and Ho–Ge systems contain isostructural phases.[115] The symmetry relationships among these bismuth units and the calcium atoms have led to a speculative assignment of valence electrons to the clusters together with considerable delocalization between the groups.[43] For example, the dimers that lie above and below and end-on to each Bi_4 square unit and at somewhat longer distances appear to be bound in a π fashion. The structure is quite complex for a rigorous bonding study, but what seems important in this and other cases is that the highest energy electrons that may be more-or-less delocalized from such a cluster derived in the limit of complete charge transfer are often more nonbonding in character and what are retained to generate a recognizable cluster are the lower lying electrons in σ bonds.

A simpler interaction in a related cluster has been perceived in Na_3Hg_2.[116] Here planar mercury units with D_{2h} and nearly D_{4h} symmetry are bridged by two groups of sodium ions that naturally exhibit the same symmetry. MO calculations show that the limiting species Hg_4^{6-} is closed-shell, although such an extreme electron transfer is, of course, quite unreasonable. However, the sodium set with the same symmetry as the highest occupied molecular orbital gives a perfect means for delocalization of some charge back onto the cations and thus into larger arrays while still retaining some σ-bonding density in the cluster. The same MO scheme naturally also applies to Bi_4^{2-} and Te_4^{2+} on the addition of eight more electrons necessary to achieve close to electroneutrality. Mercury, a kind of the magic metal when it comes to bonding, forms other compounds with the alkali metals with a variety of unprecedented polymercury species, for example, infinite ribbons in NaHg but rhomboids joined at opposite corners into chains in KHg.[117]

Although this review closes on a rather speculative note, lacking any better interpretation of some of these unusual bonding features, what seems clear at this point is that intermetallic phases may contain considerably stronger anion–cation interactions and/or higher electron chemical potentials than are achieved in most other media and that unusual results vis-à-vis more familiar molecule-like units may be expected.

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