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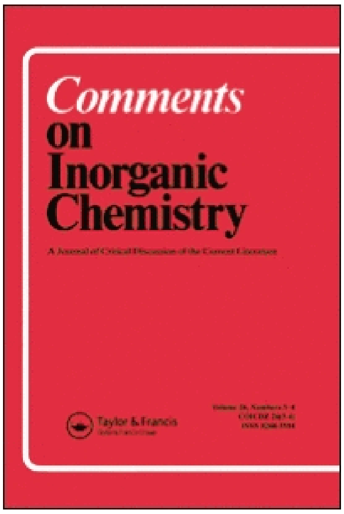

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A Rational Approach to Solid State Synthesis—The Zintl Concept

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There are a wide variety of ternary compounds, $A_xM_yX_z$, where A = alkali or alkaline earth metal, M = semimetal or main group element and X = pnictide, that have been synthesized. For example the compounds Ba_3AlSb_3, Ca_3AlSb_3, $Ca_5Al_2Sb_6$ and $Ca_{14}AlSb_{11}$ have been synthesized and their structures can be understood via the Zintl formalism which can be simply stated as the octet rule for all atoms. The structures can be generally formulated as $A^+ + [(MX)^-]$ so that the anionic units in these examples may be written as: $(Al_2Sb_6)^{12-}$; $(AlSb_3)^{6-}$ chains; a $(Al_2Sb_6)^{10-}$ network; and $[(AlSb_4^{9-}) + 4Sb^{3-} + Sb_3^{7-}]$. The Zintl concept has also been applied to ternary transition metal compounds such as the lanthanum transition metal pnictides and ternary transition metal chalcogenides. These structures and their related properties can be understood in terms of cations and complex polyatomic anionic units. The Zintl concept, as it applies to ternary pnictide compounds, will be presented and its extension to ternary transition metal pnictides will be discussed.

Key Words: *Zintl, ternary, solid state chemistry, transition metal ternary compounds, magnetic semiconductors, new materials*

INTRODUCTION

The design, synthesis and characterization of new materials are significant steps towards developing important new technologies.[1] The synthesis of new ternary and multi-ternary compounds have resulted in new properties that have or will have technological applications. Several recent examples include the synthesis and

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characterization of ternary molybdenum chalcogenides, $M_xMo_6X_8$ (M = metal, X = chalcogen, $x \sim 1$),[2] and ternary metal borides. The superconducting ternary chalcogenides have been shown to have very high critical magnetic fields and have the potential for technological application. The recent discovery[3,4] of a class of new ternary compounds typified by $Nd_2Fe_{14}B$ has resulted in new permanent magnets, and devices employing these materials were almost immediately brought into industrial production. More recently, work on multi-ternary oxides has resulted in a series of new high temperature superconductors[5-8] such as $[La(Sr)]_2CuO_4$, $YBa_2Cu_3O_{7-\delta}$ and $[Bi(Tl)]_2[Sr(Ba)]_2Ca_{n-1}Cu_nO_{2n+4}$. It is expected that new theoretical concepts[9] will be required to explain their properties and, in addition, their application may revolutionize the electronics industries. These three recent examples of new compounds with exciting properties lead to the expectation that the further study of ternary compounds and their properties is essential and will continue to change the state of science and technology in many different fields.

Although in many cases the discovery of new materials has been accidental,[10,11] several rational approaches to solid state synthesis have been proposed[11-14] and may lead to a large number of new compounds. Such a rational approach is seen in the Zintl concept[13-15] which has been applied to materials that had been considered to be intermetallic compounds,[13,16,17] to ternary transition metal chalcogenides and pnictides,[18] and to ternary lanthanide transition metal pnictides.[19] The Zintl concept can be simply stated as the octet rule for all atoms (with the exception of transition metals); electronegative elements gain as many electrons as necessary to complete their octet and the electropositive metal loses electrons. This brief review will be limited to solid state ternary compounds that contain As, Sb or Bi as one component and will outline the application of the Zintl concept to the design of these compounds.

MAIN GROUP TERNARY ZINTL COMPOUNDS

Interest in ternary Zintl compounds arises from the rich variety of solid state structures exhibited by these materials. Of particular

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interest are the one- and two-dimensional anionic substructures, which will lead to anisotropic properties, and perhaps reduced dimensionality interactions. Zintl was the first to recognize that the alkali and alkaline earth metals combine with group 14 and 15 elements to form compounds that can be considered stoichiometric salts. For example, he showed that magnesium usually combines with the metalloids of group 14 or 15 to form compounds such as Mg_3X_2(X = P, As, Sb, Bi)[20] and Mg_2X (X = Si, Ge, Sn and Pb).[21] The alkaline earth metal donates its electrons to the main group atom and the result is a structure consisting of anions with filled valence shells. If there are not enough cations to donate electrons in order to provide the main group atoms with a filled octect, then the formation of homoatomic bonds in these binary compounds provides the necessary electrons to form octects for all atoms. This interpretation of structures has been extended to ternary phases.[13,16–19] When two metalloids are combined with alkali or alkaline earth metals, a large number of compounds can be prepared that contain species directly analogous to binary anions in complex salts. This method of analyzing structures is outlined for several ternary compounds in the examples below. More detailed reviews covering many of the binary and ternary solid state Zintl compounds are found in Refs. 13, 16 and 17.

The compounds Ba_3MSb_3(M = Al, Ga)[22–24] can be described in terms of the Zintl concept. The cations are the Ba atoms, and the anions are made up of two MSb_4 tetrahedra which share a common edge to form an $M_2Sb_6^{12-}$ anion. The Ba atoms donate their charge to the polyatomic anions which use these electrons to form bonds. M is provided with one extra electron and therefore forms four bonds (similar to group 14). The Sb atoms at the common edge form two bonds similar to elements of group 16 as a result of each Sb atom acquiring one additional electron. The terminal Sb atoms form only one bond similar to halogens: so two electrons have been added. The total of 12 charges for the polyatomic anion unit are compensated for by the Ba ions. Although the Ba_3GaSb_3[24] anionic unit, $(Ga_2Sb_6)^{12-}$, is isosteric to the Ba_3AlSb_3 anionic unit, $(Al_2Sb_6)^{12-}$, they crystallize in different space groups. A portion of the unit cell of Ba_3AlSb_3 is shown in Fig. 1. The polyatomic anion $(M_2X_6)^{12-}$ is structurally similar to other anions

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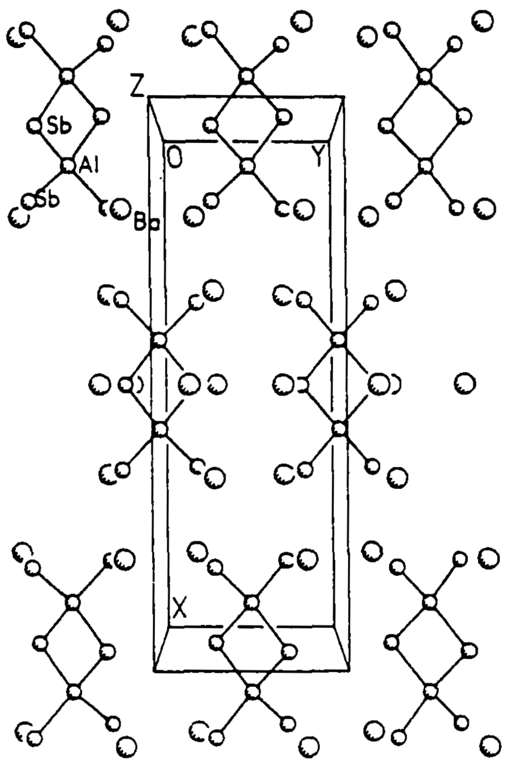

FIGURE 1 A view down the *c* axis of Ba_3AlSb_3 showing the $(Al_2Sb_6)^{6-}$ units. This view shows only ½ of the cell down *c*.

such as $Ge_2S_6^{4-}$, $P_2S_6^{2-}$, $Fe_2S_6^{6-}$ as well as to neutral molecules such as Al_2Cl_6 and Fe_2Cl_6.

When Ba is replaced by Ca in Ca_3MX_3(M = Al, Ga; X = As, Sb)[23-25] a new structure results (Fig. 2). The Ca^{2+} cation is much smaller than the Ba^{2+}, and this allows the MX_4 tetrahedra to fulfill the octet rule by forming chains instead of isolated dimeric anions. The anionic unit is now a chain made up of MX_4 tetrahedra connected by common corners ($MX_2X_{2/2}$). This type of chain linkage is often found in polyphosphates (PO_3^- chains) and polysilicates (SiO_3^{2-} chains). A new structure can be prepared if one tries to make the Ca_3MX_3 compound slightly deficient in calcium: $Ca_5M_2X_6$

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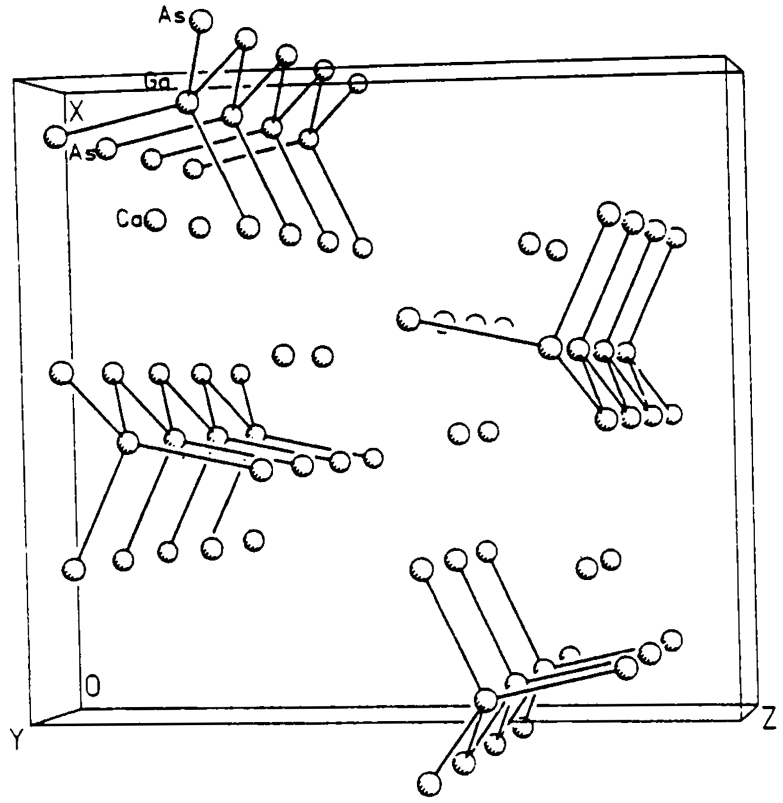

FIGURE 2 A view down the *b* axis for the unit cell of Ca_3GaAs_3. Some of the Ca^{2+} ions have been omitted for clarity.

(M = Al, Ga; X = As, Sb).[26-30] The bonding in the compound $Ca_5M_2X_6$ can also be accounted for by the Zintl concept. $Ca_5M_2X_6$ is structurally related to Ca_3MX_3 in that it is composed of MX_4 tetrahedra that are connected by common corners to form chains. Since it is deficient in Ca (and therefore electrons) compared with Ca_3MX_3, the anionic unit must form additional bonds in order to satisfy the octet rule. Two of the chains from the Ca_3MX_3 structure are connected in the $Ca_5M_2X_6$ structure by common X_2 groups to form double chains, $MXX_{2/2}(X_2)_{1/2}$, running parallel to each other in the structure (Fig. 3). With one fewer Ca^{2+} ion, the single chains of the MX_4 tetrahedra observed in the Ca_3MX_3 structure are now

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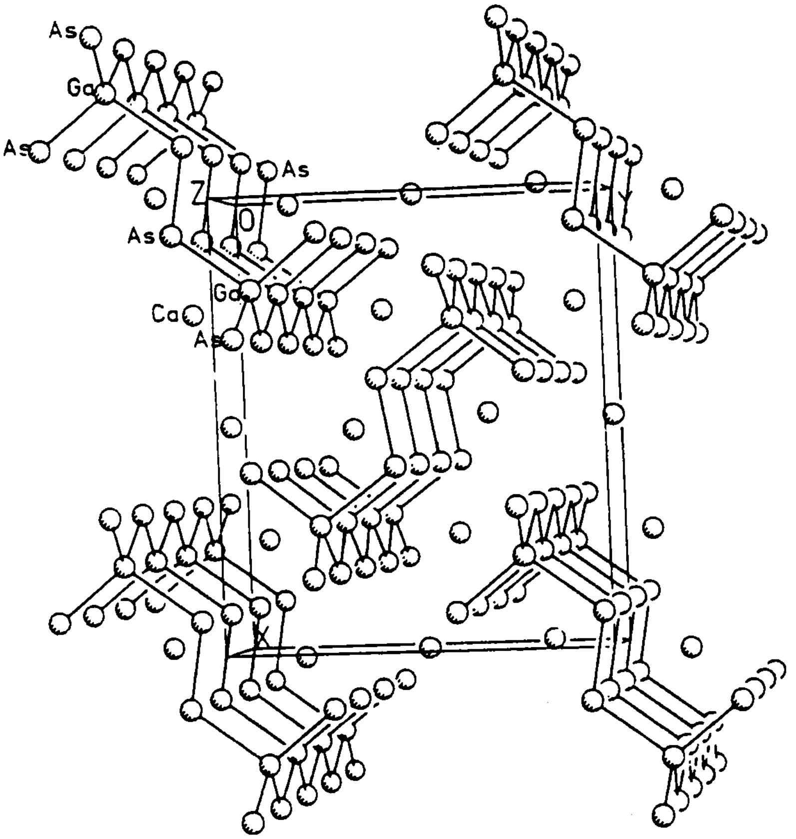

FIGURE 3 A projection down the *c* axis of Ca_5GaAs_6. Some of the Ca^{2+} ions have been omitted for clarity.

double chains in the $Ca_5M_2X_6$ structure. In order for the group 15 atoms to have enough electrons, they form homoatomic bonds. All of the structures mentioned above can be generally formulated as $nA^{m+} + [(MX)^{(n \cdot m)-}]$ so that the examples mentioned above may be written as: $6Ba^{2+} + [(M_2X_6)^{12-}]$; $3Ca^{2+} + [(MX_3)^{6-}]$ and $5Ca^{2+} + [(M_2X_6)^{10-}]$.

Another unique structure can be formed with yet another ratio of Ca:M:X: $Ca_{14}MX_{11}$ (M = Al, Ga; X = As, Sb).[31,32] The formula unit has been written as $14Ca^{2+} + [(MX_4^{9-}) + 4X^{3-} +$

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X_3^{7-}]. This structure type has an unusual three-atom pnictide linear chain, in which the Sb–Sb distance[31] is 3.196 Å compared with 2.967 Å for the As[32] chain. This linear unit is isoelectronic with I_3^-; the X_3^{7-} anion is symmetrically arranged in the solid state structure. Figure 4 shows a perspective view of the polyatomic anions in the unit cell for $Ca_{14}GaAs_{11}$.

These are just a few examples of a wide variety of structures whose bonding can be understood by distinguishing the sub-structural units which are analogous to complex anions. These structures can be rationalized according to the Zintl concept: electrons are transferred from the alkali or alkaline earth metals to the complex anions which in turn use them to form bonds, thus satisfying the octet rule.

TRANSITION METAL ZINTL COMPOUNDS

Although the bonding in ternary transition metal Zintl compounds in some cases is more complex than the simple approach outlined above, the Zintl concept can still be applied successfully. A recent example of the application of the Zintl concept to ternary transition metal pnictides is outlined below. $CaNi_2P_2$ crystallizes in the $ThCr_2Si_2$ type structure.[33,34] In this compound, the phosphorus atoms form pairs with a P–P distance of 2.207 Å. Thus the P atoms may be considered P_2 units with a P–P single bond and can be assigned a formal oxidation number of −4. Ca is assigned the oxidation num-

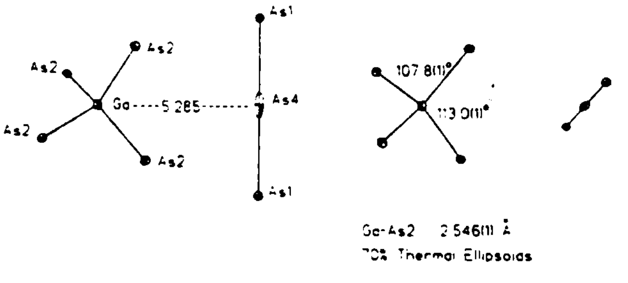

FIGURE 4 (a) A perspective view of the MX_4^{9-} and the X_3^{7-} units in $Ca_{14}GaAs_{11}$ showing their relative orientation within the unit cell.

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ber of +2. The Ni atoms, which are all equivalent, are therefore given the oxidation number +1 corresponding to the formula $Ca^{2+}Ni^{1+}Ni^{1+}[P_2]^{4-}$. This implies that the nickel in $CaNi_2P_2$ is formally a d^9 system. The P atoms around the Ni have approximately tetrahedral geometry and the 4s and 4p orbitals on Ni are involved in these "sp^3 hybrid" bonds. The electrons for these bonds have already been assigned to the P_2 pairs. Additionally, every Ni atom is also surrounded by a square of Ni atoms with Ni–Ni distances of 2.769 Å. These are considered bonding interactions and are built up of the d_{xy} orbitals of each Ni atom. The other eight electrons of each Ni atoms can then be accommodated in the 4 remaining nonbonding d orbitals. This simple bonding model accounts for the diamagnetism observed in $CaNi_2P_2$ and provides insight into the magnetic and electronic properties of this group of compounds.[33] A large number of compounds crystallize in the $ThCr_2Si_2$ (Fig. 5) structure whose bonding has been described above.[33-36] The other structure types that are observed with d^0, d^5 and d^{10} transition metals are the $CaAl_2Si_2$ and $CaMnBi_2$ structure types and variants thereof.[13,16,17] In contrast to the $ThCr_2Si_2$ structure, these structure types do not have bonded pairs of pnictides and in the case of the $CaAl_2Si_2$ structure type the pnictide is given a formal oxidation number of 3−. The $CaAl_2Si_2$ and the $CaMnBi_2$ structures are shown in Fig. 6. The interpretation of these structure by the Zintl approach[16] is not adequate to explain the bonding in these compounds, and extended Hückel theory calculations on these structures has provided a useful interpretation.[37]

Other ternary transition metal compounds that can be described by the Zintl formalism are found to have transition metals with filled d-shells such as Na_2CuSb,[38] K_2AgBi,[39] $K_3Cu_3As_2$,[40] and K_5CuSb_2.[41] All of these compounds with nearly filled d-shell transition metals display zigzag chains in their structures. The transition metal is always linearly coordinated[16,38-42] and the angles in the chains occur at the nontransitional element. These anion units tend to be largely independent of the number and type of cations embedded between them. The change in polymerization from a chain to a hexagonal net arises from a change in the number of bonds which the group 15 element possesses. This also dictates the charge on the polymeric unit.

Recently, a new series of transition metal compounds,

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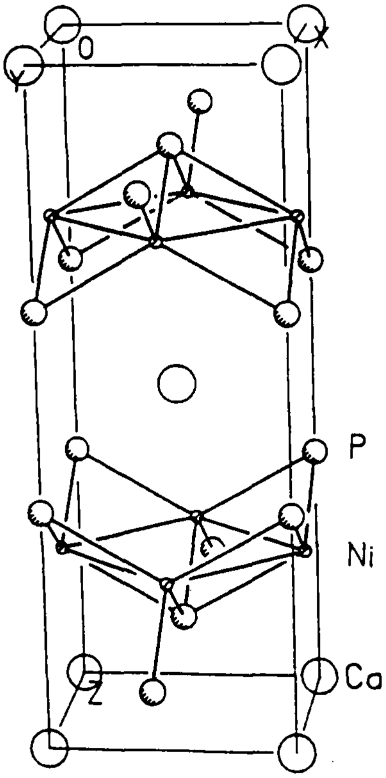

FIGURE 5 The ThCr$_2$Si$_2$ structure.

A$_{14}$MnX$_{11}$(A = Ca, Sr; X = As, Sb, Bi),[43,44] which are isostructural to the main group Zintl compounds, Ca$_{14}$MX$_{11}$, have been prepared. If the Zintl concept is used to rationalize the bonding observed in this structure type, A$_{14}$MnX$_{11}$,[43] the formal oxidation state of the Mn ion can be obtained. The analysis is identical to the main group analogues.[16,31] An oxidation state of 2+ is assigned to all the alkaline earth atoms and the isolated pnictide atoms are given an oxidation state of 3−, thus satisfying their octet. The charge on the three atom linear unit can be obtained using the VSEPR model[45]: the central atom has three lone pairs in the equatorial position similar to XeF$_2$[46] and the two terminal atoms have complete octets; thus the three atom chain has a formal charge of

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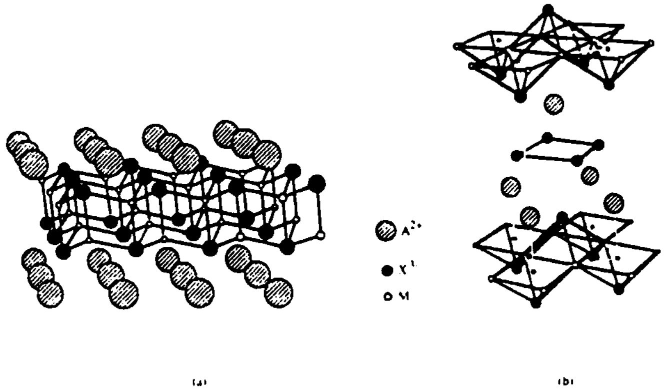

FIGURE 6 The (a) $CaAl_2Si_2$ and the (b) $CaMnBi_2$ structure type. The representations for the atoms are the same in (a) and (b).

7 −. Therefore, in one formula unit, there are fourteen A^{2+} cations, four X^{3-} anions and one X_3^{7-}, leaving a charge of 9 − on the tetrahedral MnX_4 unit. The X atoms in the tetrahedral unit can be assigned an oxidation state of 3 −; thus Mn is a 3 + ion (d^4). The compound is made up of $Mn^{III}X_4^{9-}$ tetrahedra, X_3^{7-} linear anions, and isolated X^{3-} and Ca^{2+} ions. A view of the polyatomic anions in $Ca_{14}MnBi_{11}$ is shown in Fig. 7 (important distances and angles are labeled). All the Mn–Bi distances in the $MnBi_4$ tetrahedra are the same, 2.814(1) Å, and the tetrahedron is distorted with angles of 105.4(1)° and 118.0(1)°.

The magnetic susceptibility data indicates that the oxidation state of the Mn is 3 +. The slight distortion of the Mn^{III} tetrahedron to D_{2d} symmetry results in a stable high spin d^4 configuration. In addition, although the Mn atoms are ~11 Å apart, all the compounds in the series, $A_{14}MnX_{11}$, undergo a ferromagnetic transition at ~40–65 K. Although the magnetic moment provides evidence that the Zintl concept can be used to obtain the oxidation state on the metal ion within this compound, the low temperature ferromagnetic behavior indicates that a delocalized electronic description of the solid state structure may be more appropriate. Further property measurements of these transition metal compounds will provide a better understanding of the bonding in these materials.

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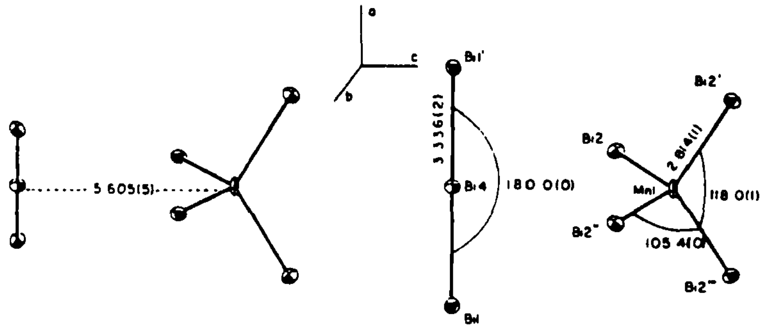

FIGURE 7 A perspective view 15° off the *b* axis of the polyatomic anions in $Ca_{14}MnBi_{11}$, showing their relative orientation within the unit cell. [Reproduced from Ref. 43.]

FUTURE OUTLOOK

The synthesis and characterization of transition metal pnictide ternary compounds present a promising area of chemistry. The new Zintl phases that have been prepared with such unconventional elements as Mn, Ni, Cu and Zn provide incentive for additional exploratory synthesis. To the extent that the Zintl ideas apply to the class of compounds considered, one has a simple set of rules which provides a mechanism for predicting new compounds and, perhaps, tailoring new physical properties. The exciting aspect of these ternary compounds arises from the variety of anionic substructures (including one-dimensional and two-dimensional lattices) which may be formed and stabilized in the solid state. Understanding the structure-property relationship of these compounds will provide the basis for designing new materials with interesting properties. The experience of the past twenty years has demonstrated that fundamentally new concepts, phenomena and technologies are discovered through such studies of new materials.

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