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Zintl Phase Variations Through Cation Selection. Synthesis and Structure of $A_{21}Cd_4Pn_{18}$ (A = Eu, Sr, Ba; Pn = Sb, Bi)

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Four new Zintl compounds, $Ba_{21}Cd_4Sb_{18}$, $Ba_{21}Cd_4Bi_{18}$, $Sr_{21}Cd_4Bi_{18}$, and $Eu_{21}Cd_4Bi_{18}$, have been synthesized and structurally characterized. Despite the similarity in their chemical formulas and regardless of their identical electronic requirements, the structures of the Ba compounds and the Sr and Eu compounds are subtly different. Due to the cations, a cleavage of a selected pnicogen−cadmium bond occurs and the structures adapt to a novel packing of the resultant heteronuclear anions.

The compounds formed between the alkali- and alkaline-earth metals and the post-transition groups 13–15 elements are typically referred to as Zintl phases.[1,2] Their structures and bonding can be rationalized with the aid of the Zintl–Klemm concept,[1,2] assuming a complete electron transfer from the less electronegative metals to the more electronegative ones so that each element achieves a closed-shell state. Recently, these ideas, particularly, the notion that the cations are just "electron donors" and/or "space fillers", have been challenged by new research, which suggest them to be intimately involved in the chemical bonding.[3–9] Our own studies on the unique cation preferences in the A_2CdSb_2 structures (A = Ca, Yb) have also demonstrated the cations' character as structure-directing factors.[9] Herein, we provide new examples for the important role of the cations in Zintl phases by reporting the synthesis and the structural characterization,[10] together with the electronic structure calculations for two new types of Zintl phases: $Ba_{21}Cd_4Bi_{18}$ and $Ba_{21}Cd_4Sb_{18}$ on one side, and $Eu_{21}Cd_4Bi_{18}$ and $Sr_{21}Cd_4Bi_{18}$ on the other. Despite the similarity in their chemical formulas and regardless of their identical electronic requirements, the structure of the Ba compounds is subtly different from that of the Sr and Eu compounds. All structures are based on corner- and edge-shared $CdSb_4$ and/or $CdBi_4$ tetrahedra that are linked together to form two different types of discrete Cd_4Pn_{12} and Cd_8Pn_{22} polyanions (Pn denotes the pnicogens Sb and Bi hereafter). They can be related to each other by breaking specific cadmium−pnicogen interactions that are intimately affected by the selection of the cations.

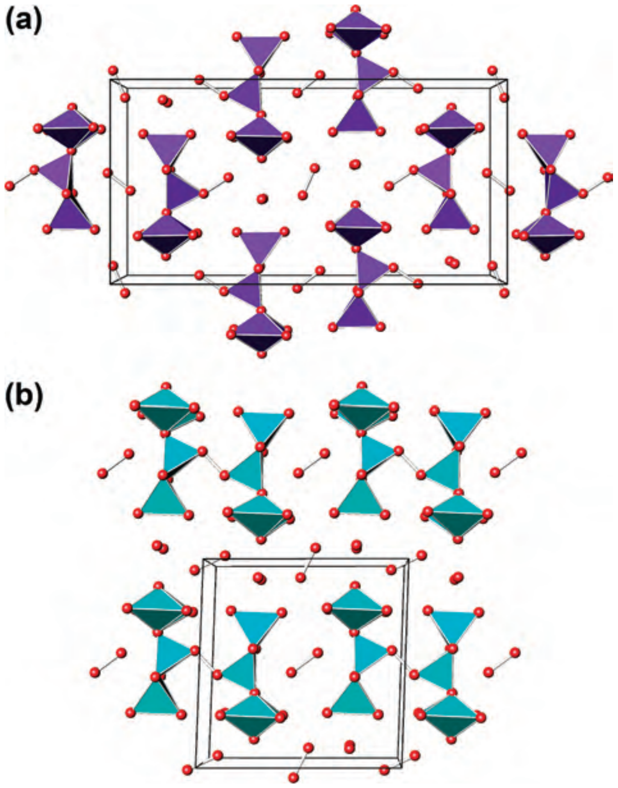

Figure 1. Side-by-side comparison of the structures of $Ba_{21}Cd_4Sb_{18}$ (a) and $Sr_{21}Cd_4Bi_{18}$ (b), drawn in polyhedral representations. The cations are omitted for clarity, and the unit cells are outlined.

$Ba_{21}Cd_4Sb_{18}$ and $Ba_{21}Cd_4Bi_{18}$ are new compounds, which crystallize in their own structure type (Figure 1 and Table

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(10) Detailed accounts of the syntheses and the crystallographic characterization are provided in Supporting Information.

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Table 1. Selected Crystallographic Data for $A_{21}Cd_4Pn_{18}$ (A = Sr, Ba, Eu; Pn = Sb, Bi) [a]

formula	$Ba_{21}Cd_4Sb_{18}$	$Sr_{21}Cd_4Bi_{18}$	$Eu_{21}Cd_4Bi_{18}$
fw (g/mol)	5525.24	6051.26	7402.4
T (K)		120(2)	
radiation, λ		Mo Kα, 0.71073 Å	
space group	*Cmce* (no. 64)	*C2/m* (no. 12)	*C2/m* (no. 12)
unit cell dimensions (Å)	$a = 18.191(6)$	$a = 18.510(4)$	$a = 18.3298(13)$
	$b = 19.103(6)$	$b = 17.685(4)$	$b = 17.4929(12)$
	$c = 37.062(10)$	$c = 18.213(4)$	$c = 17.9504(13)$
		$\beta = 92.064(4)°$	$\beta = 92.073(1)°$
V (Å^3)	12879(7)	5958(2)	5751.9(7)
Z	8	4	4
D_{calcd} (g/cm^3)	5.699	6.746	8.548
μ (cm^{-1})	212.77	729.29	787.58
$R(F^2)$ $I > 2\sigma_I$ [b]	0.0245	0.0519	0.0349
$R_w(F^2)$	0.0484	0.1146	0.0703

[a] $Ba_{21}Cd_4Bi_{18}$, $M = 7095.38$, *Cmce* (no. 64), $a = 18.438(7)$, $b = 19.303(7)$, $c = 37.66(1)$ Å, $V = 13404(14)$ Å^3. However, due to the poorer crystal quality and very high absorption coefficient, satisfactory structure refinement could not be obtained (the $R(F)$ was 0.1032). See Supporting Information for further details. [b] $R(F^2) = \Sigma F_o| - |F_c/\Sigma|F_o|$, $R_w(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]]^{1/2}$, where $w = 1/[\sigma 2F_o^2 + (A\cdot P)^2 + B\cdot P]$, where $P = (F_o^2 + 2F_c^2)/3$.

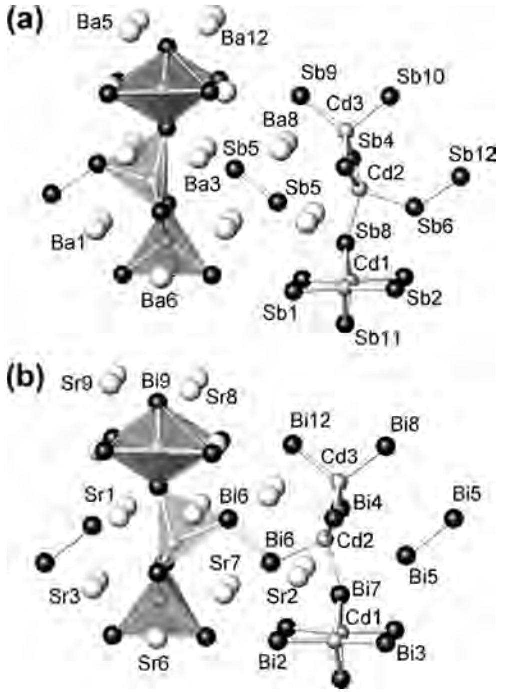

Figure 2. Close-up (combined polyhedral and ball-and-stick) views of the Cd_4Sb_{12} species in $Ba_{21}Cd_4Sb_{18}$ (a) and the Cd_8Bi_{22} in $Sr_{21}Cd_4Bi_{18}$ (b). Some of the neighboring cations are also shown, and the atoms are labeled. For relevant interatomic distances, please see the Supporting Information.

1). As can been seen from the figure, this atomic arrangement is very complicated with an unusually large unit cell containing 168 Ba cations, 32 isolated Pn anions, 8 isolated Pn_2 dimers, and 8 discrete Cd_4Pn_{12} polyanions. Following the Pearson's notation,[11] this structure type should be designated with a Pearson's symbol *oC*344, that is, a *C*-centered orthorhombic structure with a total of 344 atoms per cell. It may also represent one of the most complex, but devoid of any disorder, crystal structures of an intermetallic compound, which is solved and completely refined from single-crystal data.[11] Since the structure of the Sb analogue was established more reliably, it was chosen to be at the focus of the following discussion.

As emphasized in Figure 2, the most prominent feature of the structure of $Ba_{21}Cd_4Sb_{18}$ is the Cd_4Sb_{12} anion. This species is built of four $CdSb_4$ tetrahedra, which share both edges and corners. Three of these four tetrahedra are crystallographically unique, and the fourth one is a mirror image generated by a mirror plane perpendicular to the viewing direction in Figure 2. Such tetramers can also be described as being made of two diborane-like Cd_2Sb_6 subunits (edge-shared) that are connected through a common antimony vertex. This vertex is Sb8 in the current classification,[10] which is the only three-bonded Sb atom in this structure. Another atom that deserves special mention is Cd2. Its coordination, apparently, is prone to significant deformations due to the electrostatic potential of the neighboring cations, which can be inferred by the great distortion from the ideal tetrahedral geometry.[12] We also note that Cd2 is at the center of the only $CdSb_4$ tetrahedron that is *exo*-bonded to another Sb atom, forming a "handle" on the cluster. All Cd−Sb distances fall in the range from 2.8756(9) to 3.090(1) Å and compare well with the distances in other structures with similarly complex Cd−Sb polyanionic networks.[9,13] The Sb−Sb distance in the Sb_2 dimer, formed by a pair of Sb5 atoms, is 2.824(2) Å. The shortest contact between the Cd_4Sb_{12} cluster and the next nearest Sb_2 is 4.143(1) Å. From this point of view, dubbing these species as *isolated* is justified (Figure 1). Such a conclusion is also corroborated by the electronic structure calculations, which confirm optimized bonding interactions with an electron count that follows the Zintl rules (below).

$Sr_{21}Cd_4Bi_{18}$ and $Eu_{21}Cd_4Bi_{18}$ have the same structure as $Sr_{21}Mn_4Sb_{18}$[14] and $Ca_{21}Mn_4Sb_{18}$.[15] Despite the identical formulas, they are not isomorphous with the Ba counterparts (Figure 1). The monoclinic Sr and Eu compounds also have large unit cells with 84 cations, 16 isolated Bi anions, 6 isolated Bi_2 dumbbells, and 2 Cd_8Bi_{22} anions. These species can be viewed as dimerized Cd_4Bi_{12}, similar to those in $Ba_{21}Cd_4Bi_{18}$. This idea is emphasized in Figure 2; if the tetrahedra with the handles of two neighboring clusters in the structure of $Ba_{21}Cd_4Bi_{18}$ are allowed to distort so that the Cd centers (Cd2) are flipped in opposite directions, the resultant fragments can be bridged via the dimers to form a twice as large Cd_8Bi_{22} anion from two Cd_4Bi_{11} subunits.

What causes such differences between the structures of the Eu and Sr compounds on one hand and the Ba compounds on the other? After all, this is a case where not only the crystal packing but also the electronic requirements

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(11) (a) Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed.; American Society for Metals: Materials Park, OH, 1991; (b) Inorganic Crystal Structure Database (ICSD); FIZ Karlsruhe/NIST, 2005.

(12) Cd2 and Cd3, the center of another neighboring tetrahedron, come somewhat close at a distance of 3.099(1) Å, which the LMTO calculations show to be a very weak interaction; for COHP, see Supporting Information.

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can change as a consequence of the broken Cd−Pn bonds (examples of intermetallic compounds, including the cluster compounds, whose structures change upon substituting smaller atoms for larger ones are well-known;[1,2,7,8] however, there are very few precedents involving Zintl phases with isolated polyanions, where bonds are broken or made and the structures are "repacked" as a result of the different cations being used).[16] A careful analysis of the bonding parameters hints that cation–anion interactions may play a more important role than originally thought. This comparison is facilitated in the case of the isomorphous $Sr_{21}Cd_4Bi_{18}$ and $Eu_{21}Cd_4Bi_{18}$ since Sr^{2+} and Eu^{2+} are very similar in size. Shannon's radius of Sr^{2+} is only slightly bigger than that of Eu^{2+},[17] yet certain Cd−Bi distances and Bi−Cd−Bi angles prove important correlations. For example, in $Eu_{21}Cd_4Bi_{18}$, the Cd2−Bi6 distance is 2.977(2) Å and the Bi6−Cd2−Bi7 angle is 80.39(5)°, while the corresponding distances and angles in $Sr_{21}Cd_4Bi_{18}$ show an increase to 3.002(3) Å and 81.07(7)°, respectively. These results can be reconciled with the trends observed in $Ca_{21}Mn_4Sb_{18}$ and $Sr_{21}Mn_4Sb_{18}$, where a more significant cation effect is present (Ca^{2+} is much smaller than Sr^{2+}).[17] All of the above information is an indication that both the Cd_8Bi_{22} and Mn_8Sb_{22} species are not rigid and are very sensitive to the cation environment. It could then be expected that when bigger cations with the same charge, such as Ba^{2+}, are used, they can apply substantial "chemical pressure" on the polyanions, enough to cause significant deformations and even bond cleavage. Logically, the effect will be most noticeable where the cations are tightly coordinated, yet some more "room" can be freed if the anions were to be slightly displaced (without extensive rearrangement or changing the overall electronic requirements). This appears to be the case around the Cd2 atoms in both structures.

The last point we discuss herein is the formal valence electron count. Following the Zintl–Klemm concept,[1,2] the $Ba_{21}Cd_4Sb_{18}$ can be readily rationalized as follows: $[Ba^{2+}]_{168}\{[Cd_4Sb_{12}]^{26-}\}_8\{[Sb_2]^{4-}\}_8[Sb^{3-}]_{32}$ (considering the content of the whole unit cell). Analogous breakdown of the structure of the $A_{21}Cd_4Bi_{18}$ (A = Sr, Eu) compounds leads to $[A^{2+}]_{84}\{[Cd_8Bi_{22}]^{48-}\}_2\{[Bi_2]^{4-}\}_6[Bi^{3-}]_{16}$ (the divalent Eu cations were confirmed by magnetization measurements; see Supporting Information). From the above information, it follows that the simplistic Zintl reasoning works well for these complex structures, and this conclusion is fully corroborated by the electronic structure calculations done by the TB-LMTO-ASA method.[18] Projections of the corresponding total and partial density of states (DOS) for both structures are presented in Figure 3. As seen from the figure, the band structures are very similar, as expected, and the Fermi level in both cases falls into a small gap. This is indicative of a closed-shell system that may exhibit semiconducting behavior, as known for the typical Zintl phases.[1,2] Another important point that the calculations confirm is the importance of the cation–anion interactions. The DOS and the crystal orbital Hamilton populations (COHP) near the Fermi level are dominated by the cation's d and anion's p states. Further examination of the COHPs of all bonding interactions in the polyanionic substructure confirms that the bonding in these two structure types is fully optimized, as predicted by the Zintl reasoning.

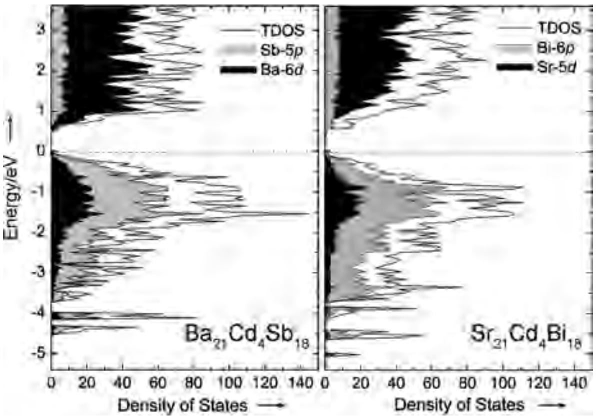

Figure 3. Density of states (DOS) for both structure types. In both cases, energy gaps at the Fermi level of about 0.5 eV are present. Shaded partial DOS show the contributions from cation's d orbitals (black) and anion's p orbitals (gray).

In conclusion, ternary Zintl phases containing d-block metals with half-filled and completely filled d-shells have generated a lot of interest due to their unique structures and physical properties.[19] With this Communication, we expanded the variety to include four new Zintl phases, whose structures, regardless of their identical chemical formulas, are similar but not identical. The results from this work complement well our previous studies on the roles of the cations as structure selection factors for related systems[9] and provide a novel example of polyanionic substructure evolution via cation substitutions.

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Supporting Information Available: Thorough experimental section, along with the crystallographic information files (CIF), computational details, and plot of the temperature dependence of the magnetic susceptibility of $Eu_{21}Cd_4Bi_{18}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Sr_2Sb_3 (*Z. Naturforsch.* **1979**, *34B*, 1162) and Sr_2Bi_3 (*Mater. Res. Bull.* **1994**, *29*, 149) are seemingly such examples; however, despite the apparent similarities, the electron count in both cases is very different and only Sr_2Sb_3 can be considered as a Zintl phase.

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(18) Jepsen, O.; Andersen, O. K. *The Stuttgart TB-LMTO Program*, version 4.7.

(19) Kauzlarich, S. M.; Brown, S. R.; Snyder, G. J *Dalton Trans* **2007**, *21*, 2099–2107.