Dalton Transactions

Accepted Manuscript

www.rsc.org/dalton

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

$K_{11}Cd_2Sb_5$ Built of Unprecedented planar $CdSb_3$ Triangle

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

The novel ternary Zintl phase $K_{11}Cd_2Sb_5$ (1) with the unusual butterfly-shaped $[Cd_2Sb_5]^{11-}$ (1a) cluster anion has been prepared by employing enhanced stoichiometric proportion of K atoms that act as a scissor. 1a is composed the two coner-shared unprecedented planar $CdSb_3$ triangles that represent the first tricoordinated example of Cd unexpected for the octet rule.

Zintl clusters have been receiving extensive and enduring interest because of their fascinating and diversified structures, intriguing chemical bonding and unique reactivity.[1] The structural diversity largely results from a huge variety of combinations between the classic binary A(AE) − E Zintl phases [A(AE) = alkali(alkaline or rare earth) metals, E = post-transition groups 13-15 elements] and transition metals M.[2-17] The varied M−E bonding and coordinating modes not only add novel structure and bonding, but also induce foreign concept and rules to the chemistry of classic Zintl phases that is usually rationalized with aid of the Zintl-Klemm concept, assuming a complete electron transfer from less electronegative A(AE) to more electronegative E to achieve a stable closed shell state or octet requirements (8−N rule). For example, our recent investigation into the K−Zn−Bi system has revealed the planar 6π e-$[ZnBi_4]^{3-}$ five-membered ring in K_6ZnBi_5 [2] and linear 16e-$[ZnBi_2]^{4-}$ trimer in K_4ZnBi_2,[3] which are isostructural and isovalent with the aromatic 6π *e*-$[HCN_4]^-$ tetrazole anion, and 16*e*-CO_2, respectively. These observations reveal that aromatic concept and 16-electron rule, which are well established in organic and triatomic systems, respectively, also play a structure-directing role in Zintl phases. We thus extend our research into the present K−Cd−Sb system. A number of ternary A(AE)−Cd−Sb Zintl phases have been reported, such as ACdSb (A = K,[4] Na [5]), $A_2AECdSb_2$,[6] $AAECd_2Sb_3$ (A = K, Na, AE = Ca, Sr, Ba, Eu, Yb),[7] AE_2CdSb_2 (AE = Yb, Ca),[8] $Ba_3Cd_2Sb_4$,[9] $AE_{11}Cd_6Sb_{12}$ (AE = Sr, Eu, Ba),[10–12] $Ba_2Cd_2Sb_3$,[13] $AE_9Cd_{4+x}Sb_9$ (AE = Ca, Sr, Yb, Eu),[14] $AECd_2Sb_2$ (AE = Ca, Sr, Ba, Eu, Yb),[15] and $Re_{21}Cd_4Pn_{18}$ (Re = Eu, Sr, Ba; Pn = Sb, Bi),[16] $AECd_{1-x}Sb_2$ (AE = La, Ce, Pr, Nd, Sm).[17] They are all composed of corner− or edge−shared $CdSb_4$ tetrahedra resulting from *sp*^{3} hybridization to fulfill both the 8-N rule of Cd (Sb) and formal charge balance of the formulae composed of A^+, AE^{2+}, Cd^{2+}, Sb^{3-} (or Sb_2^{4-} in case of balance requirement) according to Zintl-Klemm concept. Herein, we report the novel ternary K−Cd−Sb Zintl phase, $K_{11}Cd_2Sb_5$ (**1**), the first A(AE)−Cd−Sb Zintl phase that violates the 8-N rule as a consequence of the *sp*^{2}-hybridized $[CdSb_3]$ triangular unit. Similar *sp*^{2}-hybridized $ZnBi_3$ and even linear *sp*-hybridized $ZnBi_2$ units have been known, but they are stabilized by the additional Zn−Bi π electrons driven by the octet requirement of the *d*^{10} Zn centers. From this point of view, the formation of the planar $[CdSb_3]$ triangle in **1**, which disobeys the well established octet rules of Cd, is surprising because of the absence of Cd−Sb π bonds as will be described later. The synthesis, cluster and crystal structures, bonding and band analyses of **1** will be detailed below.

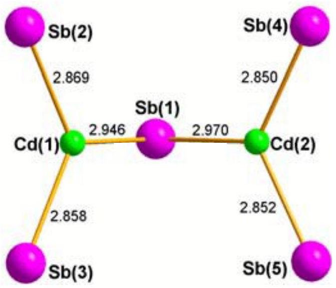


Fig. 1 Structure and bond lengths (Å) of the isolated $[Cd_2Sb_5]^{11-}$(**1a**), selected bond angles(°): Cd1–Sb1–Cd2, 84.84(4); Sb2–Cd1–Sb3, 121.82(5); Sb1–Cd1–Sb3, 118.11(4); Sb1–Cd1–Sb2, 119.21(4); Sb4–Cd2–Sb5, 122.02(4)**;** Sb1–Cd2–Sb4, 119.54(4); Sb1–Cd2–Sb5, 117.49(4).

1 was obtained as silver-gray block-shaped crystals from the solid state reaction of the stoichiometric proportion of the elements in welded niobium containers that were sealed in an evacuated fused silica jacket (20 mm i.d.) under high vacuum (ca. 10^{-3} Pa). The assembly was heated at 700℃ for 48 hours and then cooled to room temperature with the cooling rate of 5℃h^{-1} (see the details in the supporting information). The purity of **1** has been confirmed by powder X-ray diffraction as shown in Fig. S1, wherein the experimental and simulated X-ray powder diffraction patterns of **1** agree well with each other. Unlike the 1:1:1 stoichiometric proportion of the elements in the layered KCdSb composed of edge-shared $CdSb_4$ tetrahedra and $SbCd_4$ mono-capped squares, more ratio of potassium in the present $K_{11}Cd_2Sb_5$ produced the discrete ternary Zintl cluster **1**. To our surprise, it is composed of the two corner-shared planar $CdSb_3$ triangles that have not thus far been observed for the ternary A(AE)−Cd−Sb species,[4-17] indicative of versatile bonding and coordinating modes of both Cd and Sb of the K−Cd−Sb system that are believed to be cation-dependent.

X-ray structural analysis of **1** reveals that it contains eleven independent K atoms and one $[Cd_2Sb_5]^{11-}$ (**1a**) cluster anion.[18] It

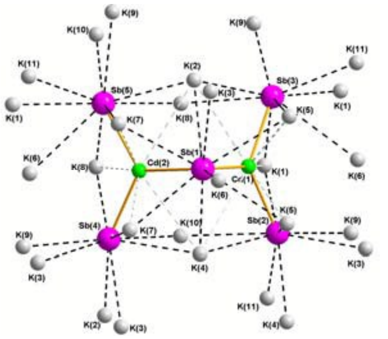
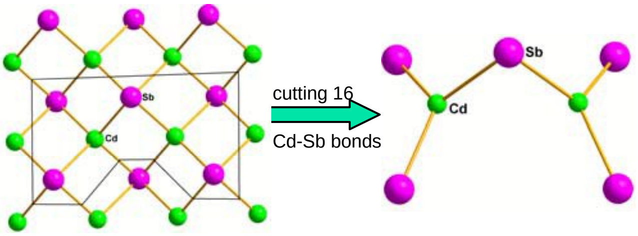


Fig. 2 Stablization of **1a** by the surrounding 29 (11 independent) K atoms.



layered sp^3-$[CdSb]^-$ isolated sp^2-$[Cd_2Sb_5]^{11-}$

Fig. 3 Formation of sp^2-$[Cd_2Sb_5]^{11-}$ by breaking the 16 Cd–Sb bonds of the $CdSb_4$ tetrahedra of sp^3-$[CdSb]^-$ as a consequence of the scissoring role of K atoms.

crystallizes in the space group $P\bar{1}$ without crystallographically imposed symmetry. The most prominent structural feature of **1** is the butterfly-shaped cluster anion **1a** that is built of the two corner-shared $CdSb_3$ triangles as displayed in Fig. 1. It is separated by eleven independent K atoms as demonstrated in Fig. 2. Unlike the layered KCdSb [4] built of $CdSb_4$ tetrahedra wherein each Sb were interacted with five K atoms, there are eight or nine K atoms coordinated to each Sb atom with a total of 29 K atoms surrounding **1a**, which serve as a scissor to cut the layered KCdSb into the isolated cluster anion shown in Fig. 3 as indicated by the shortest distance of 5.71 Å between the two adjacent **1a**. Such way of scissoring is one of numerous possibilities.[4–17] In contrast to the reported Cd−Sb species, there are up to four terminal Sb atoms and only single bridging one as a result of the largest stoichiometric proportion of K atoms thus far reported, accounting for the very unusual structural and elctronic features to be detailed later. The most significant structural feature is perfectly planar $CdSb_3$ triangles with a sum of angles around the Cd atoms close to 360° (Cd(1), 359.14(5)°, Cd(2), 359.05(4)°). Such planar Cd-centered triangles resulting from the sp^2−hybridization of Cd are unexpected for the octet rule and represent the first tricoordinated example of Cd. Of also interest is the Cd−Sb bond lengths of the $CdSb_3$ triangles in **1a** (2.850(1) − 2.970(1), av. 2.891(1) Å), which are simlar to the reported Cd−Sb single bonds (2.858 Å) in KCdSb and the other sp^3(Cd)−hybridized species (2.805−3.090 Å, ave 2.917 Å).[4–17] Of note is that these bond lengths in $[Cd_2Sb_5]^{11-}$ (**1a**) are considerably longer than those (2.76–2.83 Å) in organometallic species[19] because of the larger covalent bonding radius of the former atoms caused by the highly negative cluster charge. This indicates that, differing from the case of the $[ZnBi_3]$ triangles of the aromatic K_6ZnBi_5 [2] wherein the Zn−Bi bonds are markedly shorter than a Zn−Bi single bond because of the Zn−Bi π bonds, there is no significant Cd−Sb π bonding in the the $[CdSb_3]$ triangles of **1a**.

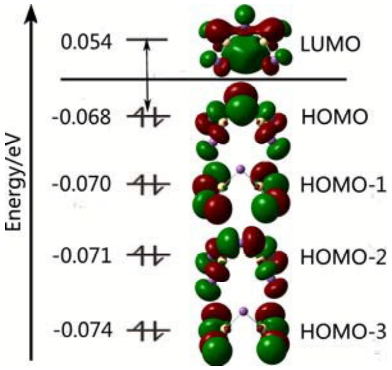


Fig. 4 Frontier molecular orbitals of **1a**.

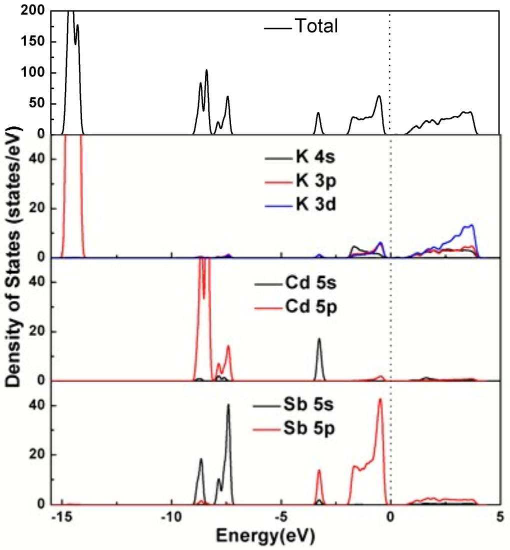


Fig. 5 Total and partial density of states of **1**.

This is also confirmed by the detailed bonding analyses between Cd and Sb to be described later. Of note is that Zn(Cd)−Pn multiple bonds such as those in the linear triatomic 16e−$[Pn{=}Zn(Cd){=}Pn]^{4-}$ (Pn = P,[20] As,[21] Bi [3]) species have been known, but those with Zn(Cd)−Sb multiple bonds have not been reported. This observation reveals that, unlike the congeners P, As and Bi, Sb is much more difficult to form π bonding as in the case of **1a**. As a consequence, all Zn(Cd)−Sb species thus far reported have $Zn(Cd)Sb_4$ tetrahedra to meet octet requirements. From this point of view, the formation of the planar sp^2-hybridized $[CdSb_3]$ triangles of **1**, which is not supported by the Cd−Sb π bonding as in the case of $[ZnBi_3]$,[2] is very unusual. The formation of **1** presents the first example wherein the formal charge balance and octet requirements are not be fulfilled simultaneously. Clearly, the former is preferred in the case of **1** to be detailed below. As in the case of the reported Cd−Sb Zintl phases, the formal charge balance of **1** can be achieved by using the Zintl-Klemm concept that gives the oxidization state assignment of $K^{+}{}_{11}Cd^{2+}{}_{2}Sb^{3-}{}_{5}$. However, the real covalent Cd−Sb bonding nature as revealed by their similar electronegativity (Cd, 1.69, Sb, 2.05) with the difference (0.36) much smaller than 1.7 for a typical ionic bond, indicates that **1** has four terminal Sb^{2-} (Sb2−Sb5) and one bridging Sb (Sb1) that is usually treated as Sb^- [4–17], which get a total of nine electrons from the surrounding nine independent K atoms, to fulfill their closed−shell electronic configuration. Hence, there is one electron available for each Cd center from the remaining two K atoms. However, unlike the case of the reported A(AE) − Cd − Sb species$^{4-17}$ built of *sp*^{3} −hybridized $CdSb_4$ tetrahedra wherein the Cd center forms four Cd−Sb σ and dative (receiving a pair of electrons from Sb) bonds to achieve its stable octet requirement, each Cd atom of **1** with a total of three electrons adopts *sp*^{2} hybridization to form three Cd−Sb σ bonds without the fourth Sb→Cd dative bonding, responsible for the formation of the unprecedented planar tricoordinated Cd unexpected for the octet rule. Of note is that, although bridging Sb is commonly treated as Sb^- [4–17] to give the charge-balanced $K^{11+}(Cd^-Sb_2^{4-})_2Sb^-$ assignment as described above, it appears as Sb^{3-} to lead to the assignment of $K^{11+}(Cd^0Sb_2^{4-})_2Sb^{3-}$ with two $Sb^{3-}\rightarrow Cd^0$ dative bonds can not be ruled out, which is supported by the significantly longer bond lengths between the bridging Sb and Cd atoms (Sb(1)−Cd(1), 2.946(1), Sb(1)−Cd(2), 2.970(1) Å, av. 2.958(1) Å) than the other four Cd−Sb bonds (2.850(1) − 2.869(1), av. 2.857(1) Å). Such inconsistence between formal charge balance requirements and the octet rules has not been observed for the known A(AE)−Cd−Sb species. It is of note that such inconsistence has also been observed for the electron-rich metal salt K_6ZnBi_5 [2] wherein the aromatic and octet requirements are achieved by the appearance of one delocalized electron: $6K^+ + [ZnBi_5]^{5-} + e^-$. However, it is not the case for the diamagetic **1**, which keeps the formal charge balance at the cost of the 8-N exception of Cd.

To examine the Cd−Sb π bonds in **1a**, the DFT calculations on the B3LYP/Lanl2dz level of *Gaussian 03* [22] using a polarizable continuum model [23] have been carried out. The frontier molecular orbitals (HOMO − HOMO-3) of **1a** wherein π bonding may exist are shown in Fig. 4. Obviously, unlike the case of the aromatic K_6ZnBi_5 [2] having a similar planar $ZnBi_3$ triangle, these frontier molecular orbitals feature Cd−Sb σ bonding and/or non-bonding orbitals, and the anticipated Cd−Sb π bonding is not observed. This is further supported by the VASP [24] using the projector augmented wave [25] method as shown in Fig. 5. As demonstrated in the PDOS curve, the bands between –2.1 eV and the Fermi level are dominated by Sb 5*p*–orbitals with a little contribution from K 4*s*–, 3*p*– and 3*d*–orbitals, revealing their non–bonding orbital character and significant K–Sb interactions. The absence of Cd–Sb π-bonding that is expected to appear in this energy range is consistent with the *Gaussian* calculation results as described above. The bands from –3.5 to –2.1 eV are mainly composed of Sb 5*p*–orbitals and Cd 5*s*– and 5*p*–orbitals, accounting for the Cd–Sb σ–bonding.

In conclusion, the novel ternary Zintl cluster $K_{11}Cd_2Sb_5$ (**1**) with the unprecedented butterfly-shaped $[Cd_2Sb_5]^{11-}$(**1a**) cluster anion has been successfully prepared from K–Cd–Sb system, revealing the promising potential of the enhanced stoichiometric proportion of K atoms acting as a scissor to break Cd–Sb bonds and produce a variety of unusual cluster anions. The triangular $[CdSb_3]$ cluster units of **1a** represents the first tri-coordinated example of Cd, which is unexpected for the octet rule and has never been observed both in coordination and in solid-state chemistry.

This work was supported by the National Natural Science Foundation of China (Grant # 21473200).

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† Electronic supplementary information (ESI) available: X-ray powder diffraction, details of experiment and theoretical calculations, crystallographic data. ICSD 425646. For ESI and crystallographic data in CIF or other electronic format see See DOI: 10.1039/b000000x/

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18 Crystallographic data of **1**: a = 9.913(1), b = 12.012(2), c = 12.849(2) Å, α = 103.570(4), β = 97.304(3), γ = 107.615(4)°. V = 1384.8(3) $Å^3$, Z = 2, ρ = 3.030 g cm^{-3}. T = 293(2) K, space group $P\bar{1}$ (No. 2), 8285 reflections measured, 4379 independent reflections (R_{int} = 0.0538), final R_1 = 0.0430 [$I > 2\sigma(I)$], final $wR(F^2)$ = 0.1134 [$I > 2\sigma(I)$], goodness of fit on F^2 = 1.066.

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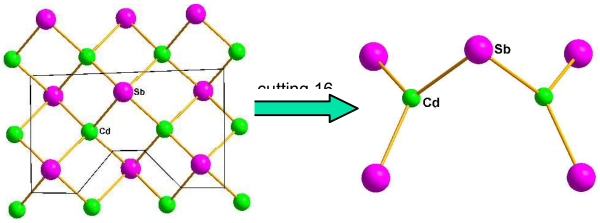

Novel $K_{11}Cd_2Sb_5$ resulting from cutting Cd–Sb bonds by K as a scissor has been prepared, which represents the first tricoordinated example of Cd unexpected for the octet rule.