Inorganic Chemistry
Communication
pubs.acs.org/IC

$Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$: Enantiomorph-like Zintl Compounds

Xiao-Cun Liu, Ming-Yan Pan, Sheng-Qing Xia,* and Xu-Tang Tao

State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan, Shandong 250100, Peoples Republic of China

Ⓢ *Supporting Information*

ABSTRACT: Two new chiral Zintl compounds, $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, were synthesized from tin-flux reactions, and the structures were determined by using single-crystal X-ray diffraction. Both compounds crystallize in the trigonal space group $R3$ (No. 146, $Z = 3$) with the anion structures containing various units: dumbbell-shaped $[Sn_2As_6]^{12-}$ dimers, $[SnAs_3]^{7-}$ triangular pyramids, and isolated As^{3-} anions. Very interestingly, these two compounds exhibit opposite chirality in the observed crystal structures, resembling enantiomorphs. Detailed structure analyses suggest possible steric effects among the anion clusters, and on the basis of the calculated electronic structures, substantial electron lone pairs exist on the anions of both compounds, which may provide a hint to understanding the origination of chirality in these intermetallic compounds.

Chirality has been the focus of many researches since it was first discovered on molecules by Pasteur in 1848.[1−4] The whole biological world seems to be excludingly constructed through homochiral molecules, such as dextrorotatory DNA double helices and amino acids.[5,6] This phenomenon implies that the stereoconfiguration of chiral materials should be crucial in affecting the corresponding physical and chemical properties. However, the utilization of such materials is seriously hampered by the synthesis of "customized" chiral compounds. Until now, although the geometrical principles of chirality have been fully understood, control of the chirality on specific compounds is still a very challenging problem. The affecting factors are complex, including the external[7−11] (such as temperature, pressure, and pH) and internal[12−15] (steric and electronic effects) ones. Notably, most of these studies are based on the organic or metal−organic compounds, while inorganic chiral materials, especially for intermetallics, were rarely reported. However, the potential applications of inorganic chiral materials have been frequently demonstrated on optical devices, adsorption separation, and asymmetric catalytic reactions.[16−18]

Herein, we report two new chiral Zintl compounds, $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$. Zintl phases are polar intermetallics usually formed by metals with very different electronegativities.[19] According to the Zintl−Klemm concept, they are charge-balanced compounds if one counts the electrons by using the octet rule. Indeed, in both compounds, there are a total of 42 Sr^{2+} or Eu^{2+} cations, 3 dumbbell-shaped $[Sn_2As_6]^{12-}$ dimers, 3 $[SnAs_3]^{7-}$ trigonal pyramids, and 9 isolated As^{3-} anions in the unit cell. Thus, their formulas can be easily rewritten as $[Sr^{2+}]_{14}[Sn^0]_2[Sn^-][As^{2-}]_9[As^{3-}]_3$ and $[Eu^{2+}]_{14}[Sn^0]_2[Sn^-][As^{2-}]_9[As^{3-}]_3$. With such a rationalization, the structures of these compounds seem to be explicitly understood and, in addition, it is very certain to believe that $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$ should be both isostructural and isoelectronic. However, in spite of the high similarity between these two compounds, their observed chiral structures are different.

The crystal structures of $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$ are compared adjacently in Figure 1 with various representations. The coordination geometries of Sr and Eu cations are provided in Figure S3. The local environments of the corresponding cations of both compounds are very similar. As indicated in the picture, mirror symmetry can be easily identified if all cations are ignored. This feature makes $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$ resemble enantiomorphs very much, as is often observed in organic compounds. In order to obtain a better illustration on the structure chiralities, polyhedral representations are provided with As1 and As4 atoms hypothetically connected along the *c* axis. In this way, various double helices are built and obviously, by the mirror symmetry, the spiral directions of these helices are opposite between these two compounds. It should be addressed here that, although such sinistral or dextral arsenic double helices do not really exist (they are not really covalently bonded), they clearly show the spiral packing manners of the $[Sn_2As_6]$ dimers and $[SnAs_3]$ trigonal pyramids, which are critical in the construction of chiral structures in $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$. Hence, detailed analyses on the anions are carried out below in order to better understand the chirality origination of these structures.

As plotted in Figure 2, the $[Sn_2As_6]^{12-}$ dimers are very special in their coordination geometry. Although similar dimeric units have been observed in Zintl phases[20−22] and the corresponding Sn−As bonds [2.6079(9)−2.6502(14) Å] also fall into the reasonable range, the $[Sn_2As_6]^{12-}$ dimers in $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$ are obviously more distorted compared to the other analogues.[23,24] This argument is supported by the detailed comparison on the corresponding dihedral angles. For example, the smallest P−SnSn−P dihedral angle of the $[Sn_2P_6]$ dimer in Ba_3SnP_3 is 57.81°,[25] very close to 60° for an ideal H−CC−H dihedral angle in a staggered ethane molecule, whereas for $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, the As_2−Sn_2Sn_1−As_4 dihedral angles in $[Sn_2As_6]$ dumbells are only 36.18° and 36.64°, respectively. Such highly distorted, isolated $[Sn_2As_6]$ anions are extremely rare in Zintl analogues because obvious steric effects can be expected.[26] Another unusual aspect of these structures is related to the isolated $[SnAs_3]^{7-}$ trigonal pyramids. Compared to $[Sn_2As_6]^{12-}$ dimers, the Sn−As bonding distances of $[SnAs_3]^{7-}$

Received: May 20, 2015
Published: September 11, 2015

DOI: 10.1021/acs.inorgchem.5b01145
Inorg. Chem. 2015, 54, 8875−8877

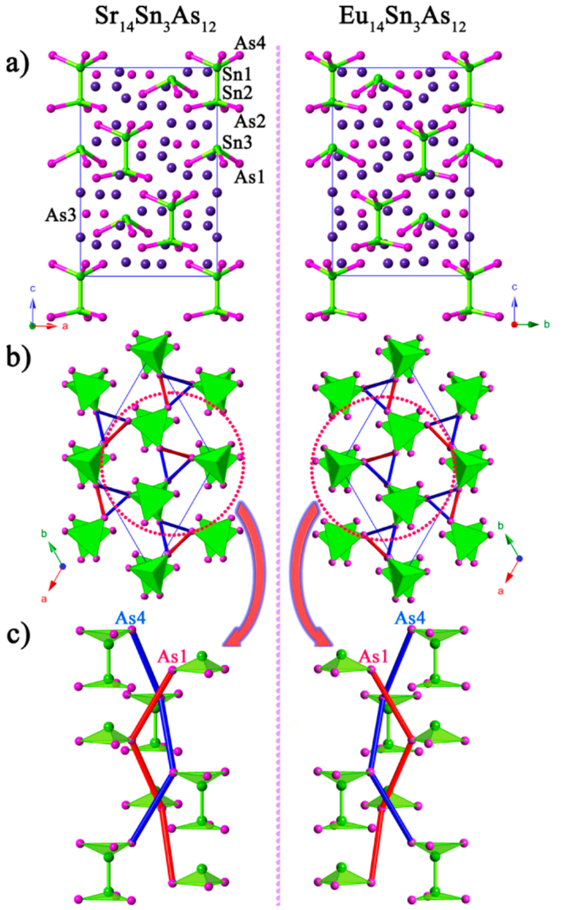

Figure 1. Side-by-side comparison of various structure representations for $Sr_{14}Sn_3As_{12}$ (left) and $Eu_{14}Sn_3As_{12}$ (right). (a) Ball-and-stick view of the crystal structure for each compound. Sr/Eu, Sn, and As atoms are indicated as purple, orange, and green spheres, respectively, and anion atoms in $Sr_{14}Sn_3As_{12}$ are labeled. (b) Polyhedral view of the anion structures, viewed along the *c* axis. The As1 and As4 atoms among these polyhedra are hypothetically linked to indicate the chiralities of the anion structures. The As1 and As4 spiral arrangements are discriminated by red and black lines. (c) Stacking of $[Sn_2As_6]^{12-}$ dimers and $[SnAs_3]^{7-}$ anions clearly showing the opposite spiral directions between these two compounds.

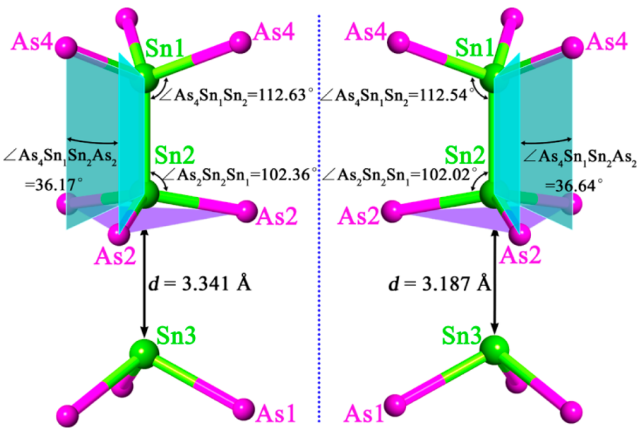

Figure 2. Anion structural representations of $Sr_{14}Sn_3As_{12}$ (left) and $Eu_{14}Sn_3As_{12}$ (right), showing the obvious distortion related to $[Sn_2As_6]^{12-}$ and $[SnAs_3]^{7-}$ clusters.

anions are obviously much longer [2.7739(9) and 2.7972(15) Å for $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, respectively]. The distances between the neighboring $[Sn_2As_6]^{12-}$ and $[SnAs_3]^{7-}$ anions can be measured by the vertical lines between the Sn3 atom and the As2 plane, which are about 3.342 and 3.187 Å for $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, respectively, as indicated in Figure 2. Although these values do not mean significant bonding interactions, they may be a hint for the existence of some weak interactions. More evidence can be found by comparing some specific bonding angles: for example, the bonding angles of ∠As4Sn1Sn2 are 112.63(3)° and 112.54(4)° in $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, respectively, not very distorted compared to the ideal tetrahedral coordination geometry; however, for ∠As2Sn2Sn1, the angles are only 102.36(3)° and 102.02(5)° in $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, respectively, about 10° smaller compared to ∠As4Sn1Sn2 in each compound mentioned above. These results obviously suggest that the As2 atoms of Sn_2As_6 trigonal antiprisms are repelled by the neighboring $SnAs_3$ trigonal pyramids, which may provide an explanation for the chirality origination of these structures. In fact, chirality related to steric and electronic effects has been well reported for many organic compounds.[27,28] Thus, it is very interesting to observe such phenomena in pure inorganic materials. In addition, these unique structural features may also correspond to unusual electronic structures, which will be discussed below.

These interesting crystallographic results require an in-depth analysis on the corresponding electronic structures of these compounds. The charges on Eu cations can first be examined by using the magnetic susceptibility measurements on $Eu_{14}Sn_3As_{12}$, as provided in Figure S4. The antiferromagnetic transition appears with a Néel temperature of about 7 K. The inverse susceptibility ($1/\chi$) curves are linearly dependent on the temperature over the range of 30−300 K. The data can be fitted to the modified Curie−Weiss law $\chi(T) = C/(T - \theta)$, where C is the Curie constant and θ is the Weiss constant.[29] The effective moment μ_{eff} calculated for each Eu cation is 7.935 μ_B, in good agreement with the theoretical value of 7.937 μ_B for a divalent Eu^{2+} ion. These results seem to provide some support on the rationalization of these compounds based on simple electron counting. However, the role of the anions in the formation of such chiral structures is still not fully understood, which should be further analyzed with the aid of theoretical calculations.

The calculated electron localization function (ELF) plots of $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$ are shown in Figure S5. For Sn−Sn bonds in $[Sn_2As_6]^{12-}$, electrons are predominantly localized between Sn1 and Sn2 atoms. However, for Sn−As pairs, the situation is subtly different and the electrons seem to be substantially populating the As atoms. This discrepancy can be explained by the obvious electronegativity difference between Sn and As atoms, which may lead to strong polarization in the Sn−As bonds. In addition, the ELF plots also indicate extensive electron lone pairs on As atoms for both compounds. Similar results can be found for the Sn−As bonds in $[SnAs_3]^{7-}$ anions. However, a high density on Sn3 atoms also strongly suggests the existence of lone pairs. The calculated total and partial density of states (TDOS and PDOS) as well as the crystal orbital Hamilton population (COHP)[30] curves can provide more details on the electronic structures. As illustrated by $Sr_{14}Sn_3As_{12}$ in Figure S6, the mixing between Sn and As obviously contributes to strong bonding interactions over the energy range of −3.85 to −2.25 eV. However, from −2.25 eV to Fermi level, the interactions are rather weak, exhibiting nonbonding or even antibonding character, especially for the Sn3−As1 bond. These theoretical analyses support the crystallographic data that the Sn3−As1 bond is much longer compared to the Sn1−As4 and Sn2−As2 ones. More importantly, the fact that there are substantial nonbonding interactions below the Fermi level further supports the ELF results, which clearly indicate the existence of electron lone pairs on Sn3 and As atoms.

With the above theoretical discussions, the repulsion between $[Sn_2As_6]^{12-}$ and $[SnAs_3]^{7-}$ can now be imagined. The electron lone pairs localized on the Sn3 and As2 atoms should play a critical role in affecting the distortion of these anion clusters, which thus provide similar steric effects, as often proven by the organic chiral materials.[31,32] Further evidence can be found from the Milliken charge population on various constituent atoms (Table S3). The charges on Sn3 atoms seem to be highly influenced by the cations: in $Sr_{14}Sn_3As_{12}$, the charge of Sn3 is 0.23−, whereas it is only 0.03− in $Eu_{14}Sn_3As_{12}$ (note that these values are not suitable for quantitative analysis because of the arbitrary distribution of the overlapped electron densities). The decreased charge of Sn3 also corresponds to the closer distance between $[Sn_2As_6]^{12-}$ and $[SnAs_3]^{7-}$ anions if referring to the structure analyses above, which is additional proof of a steric effect. However, explaining the reason for the chirality difference between these two compounds is rather difficult because it may be related to more complicated electronic effects. Moreover, although current observations only indicate one type of handedness for Sr- or Eu-containing compounds (even with more single-crystal data collections), it is still hard to conclude whether there exist other charity-different enantiomorphs or not.

In conclusion, two new ternary chiral Zintl compounds, $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$, were synthesized and reported. In spite of the similar chemical formulas and same space groups of the crystals, the packing structures of these two compounds have opposite spiral directions, similar to those organic enantiomorphs. Detailed structure analyses incorporated by theoretical calculations with DFT methods indicate that steric effects among the anions should play an important role in the chirality origination of these materials. Although chirality related to steric effects has been frequently demonstrated in the organic compounds, it is still very interesting to discover such a new phenomenon in the intermetallic system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01145.

Synthesis, crystallographic data, graphical representations of the Sr and Eu coordination polyhedra, details of measurements and DFT calculations, and powder XRD analysis, magnetic susceptibility measurements, and EDX results of $Eu_{14}Sn_3As_{12}$ (PDF)

X-ray crystallographic files in CIF format for $Sr_{14}Sn_3As_{12}$ and $Eu_{14}Sn_3As_{12}$ (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: shqxia@sdu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 51271098 and 51321091).

■ REFERENCES

(1) Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2008**, *108*, 1−73.

(2) Feringa, B. L.; van Delden, R. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 3418−3438.

(3) Ogoshi, H.; Mizutani, T. *Acc. Chem. Res.* **1998**, *31*, 81−89.

(4) Pasteur, L. *Comp. Rend. Paris* **1848**, *26*, 535−538.

(5) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737−738.

(6) (a) Ulbricht, T. L. V. *Origins Life* **1981**, *11*, 55−70. (b) Milton, R. C. de L.; Milton, S. C. F.; Kent, S. B. H. *Science* **1992**, *256*, 1445−1448.

(7) (a) Kato, T. *Science* **2002**, *295*, 2414−2418. (b) Kanie, K.; Yasuda, T.; Ujiie, S.; Kato, T. *Chem. Commun.* **2000**, 1899−1900.

(8) Tashiro, R.; Sugiyama, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 6018−6020.

(9) Inoue, Y.; Matsushima, E.; Wada, T. *J. Am. Chem. Soc.* **1998**, *120*, 10687−10696.

(10) (a) Kaneda, M.; Asaoka, S.; Ikeda, H.; Mori, T.; Wada, T.; Inoue, Y. *Chem. Commun.* **2002**, 1272−1273. (b) Kaneda, M.; Nakamura, A.; Asaoka, S.; Ikeda, H.; Mori, T.; Wada, T.; Inoue, Y. *Org. Biomol. Chem.* **2003**, *1*, 4435−4440.

(11) Nishino, H.; Kosaka, A.; Hembury, G. A.; Matsushima, K.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **2002**, *3*, 582−590.

(12) Corey, E. J.; Helal, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1986−2012.

(13) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353−3361.

(14) Borovkov, V. V.; Lintuluoto, J. M.; Inoue, Y. *J. Am. Chem. Soc.* **2001**, *123*, 2979−2989.

(15) Wolf, C. *Chem. Soc. Rev.* **2005**, *34*, 595−608.

(16) Velluz, L.; Legrand, M.; Grosjean, M. *Optical Circular Dichroism*; Academic Press: New York, 1965.

(17) Gillard, R. D.; da Luz de Jesus, J. D. P. *J. Chem. Soc., Dalton Trans.* **1979**, 1779−1782.

(18) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756−768.

(19) Kauzlarich, S. M., Ed. *Chemistry, Structure, and Bonding of Zintl Phases and Ions*; VCH Publishers: New York, 1996.

(20) Eisenmann, B.; Schäfer, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 490−491.

(21) Eisenmann, B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1982**, *484*, 142−152.

(22) Khatun, M.; Stoyko, S. S.; Mar, A. *Inorg. Chem.* **2014**, *53*, 7756−7762.

(23) Eisenmann, B.; Jordan, H.; Schäfer, H. *Z. Naturforsch., B: J. Chem. Sci.* **1984**, *39*, 1151−1153.

(24) Lam, R.; Mar, A. *Solid State Sci.* **2001**, *3*, 503−512.

(25) Eisenmann, B.; Jordan, H.; Schäfer, H. *Z. Naturforsch., B: J. Chem. Sci.* **1983**, *38*, 404−406.

(26) Bickelhaupt, F. M.; Baerends, E. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 4183−4188.

(27) Ghosn, M. W.; Wolf, C. *J. Am. Chem. Soc.* **2009**, *131*, 16360−16361.

(28) Superchi, S.; Casarini, D.; Laurita, A.; Bavoso, A.; Rosini, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 451−454.

(29) Kittel, C. *Introduction to Solid-State Physics*, 7th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 1996.

(30) Dronskowski, R.; Blöchl, P. E. *J. Phys. Chem.* **1993**, *97*, 8617−8624.

(31) Kim, S.-G.; Kim, K.-H.; Jung, J.; Shin, S. K.; Ahn, K. H. *J. Am. Chem. Soc.* **2002**, *124*, 591−596.

(32) Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353−3361.