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# The solvothermal synthesis and characterization of quaternary arsenic chalcogenides CsTMAsQ<sub>3</sub> (TM = Hg, Cd; Q = S, Se) using Cs<sup>+</sup> as a structure directing agent: from 1D anionic chains to 2D anionic layers†

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Four new quaternary transition metal arsenic chalcogenide Cs–TM–As–Q compounds (TM = Hg, Cd; Q = S, Se) were synthesized using different mixed solvents. A 1,4-diaminobutane(1,4-dab)/water mixed solvent system was used to solvothermally synthesize the selenoarsenates CsTMAsSe<sub>3</sub> (TM = Hg (1), Cd (2)). In 1, the eight-membered ring anion chain consists of trigonal-planar [HgSe<sub>3</sub>] and trigonal-pyramid [AsSe<sub>3</sub>]. Compound 2 is similar to the eight-membered ring chain anion of compound 1, and [CdAsSe<sub>3</sub>]<sup>−</sup> further joins, through μ<sub>3</sub>-Se and Cd, to form the layer anions [CdAsSe<sub>3</sub>]<sup>−</sup>. A 2-diaminopropane (1,2-dap) and water mixed solvent system was used to synthesize two thioarsenates, Cs<sub>2</sub>TM<sub>2</sub>As<sub>2</sub>S<sub>6</sub> (TM = Cd (3), Hg (4)). Compounds 3, 4 and 2 are isostructural; the Cd and Hg atoms are four coordinated. Compounds 1–4 utilize Cs<sup>+</sup> cations as a structural directing agent. Finally, the structural and optical properties of the novel series of arsenic chalcogenides were characterized.

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## 1 Introduction

Crystalline chalcogenides have attracted extensive research interest owing to their fascinating structures and their potential applications in the fields of photoelectrochemistry,<sup>1–3</sup> magnetism,<sup>4</sup> nonlinear optics,<sup>5</sup> ion exchange,<sup>6,7</sup> semiconductors<sup>8</sup> and so on. Generally, chalcogenides can be prepared using several traditional methods, including a high temperature solid-state approach, molten flux methods, electrochemical methods and hydrothermal thermal methods.<sup>9–11</sup> Since the study by Bedard *et al.*<sup>12</sup> was published in 1989, the solvothermal synthesis of main-group chalcogenidometalates using amines has attracted extensive attention, as it is a significant method for the synthesis of chalcogenides.<sup>1,9</sup> During the past few decades, owing to the diversity of the bonding modes of the chalcogen atoms, the stereochemical effect of the lone electron pairs and the various coordination orientations of As/Sb(III) by sulfur/

selenium atoms, large structural and compositional diversities have been observed for multinary chalcogenides, and therefore a large number of metal chalcogenides compounds have been prepared. Recently, it has been reported that in the combination of the structural units of As<sub>3</sub>Q<sub>3</sub> (Q = S, Se) the As<sup>III</sup> ions tend to adopt the diverse AsQ<sub>n</sub> (Q = S, Se) (*n* = 3–6) ligands that can share corners and/or edges with transition metal ions (TM = Ag<sup>+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>),<sup>11,13–24</sup> and could form interesting structural various multinary chalcogenides,<sup>8</sup> such as 1D chains, 2D layers, 3D framework. For example, RbAg<sub>2</sub>As<sub>3</sub>Se<sub>6</sub>,<sup>10</sup> NaAg<sub>2</sub>As<sub>3</sub>·H<sub>2</sub>O,<sup>13</sup> (NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>)AgAs<sub>4</sub>,<sup>14</sup> CsAgAs<sub>2</sub>Se<sub>4</sub>,<sup>15</sup> K<sub>2</sub>AgAs<sub>3</sub>Se<sub>6</sub> and Rb<sub>2</sub>AgAs<sub>3</sub>Se<sub>6</sub>,<sup>16</sup> [Ni(dap)<sub>3</sub>]<sub>4</sub>[As<sub>10</sub>Cu<sub>2</sub>S<sub>18</sub>],<sup>17</sup> [enH][Cu<sub>3</sub>As<sub>2</sub>S<sub>5</sub>],<sup>18</sup> Na<sub>2</sub>(H<sub>2</sub>dap)<sub>0.5</sub>[Cu<sub>8</sub>(μ<sub>8</sub>-Se)(AsSe<sub>4</sub>)<sub>6/2</sub>],<sup>19</sup> [pipH<sub>2</sub>][Mn<sub>2</sub>As<sub>2</sub>S<sub>6</sub>]<sup>20</sup> and [Mn(en)<sub>3</sub>]<sub>2</sub>[Mn(en)<sub>2</sub>AsS<sub>4</sub>][As<sub>3</sub>S<sub>6</sub>].<sup>21</sup> There have been comparatively few reports on the incorporation of the transition metals Cd and Hg into the framework of the main-group metal chalcogenides by means of solvothermal synthesis. For example, Cs<sub>2</sub>HgSb<sub>4</sub>S<sub>8</sub> and Cs<sub>2</sub>Hg<sub>2</sub>Sb<sub>2</sub>Se<sub>6</sub>,<sup>3</sup> Rb<sub>8</sub>[Cd<sub>2</sub>(AsS<sub>4</sub>)<sub>2</sub>(AsS<sub>5</sub>)<sub>2</sub>],<sup>25</sup> (Ph<sub>4</sub>P)<sub>2</sub>[Hg<sub>2</sub>As<sub>4</sub>S<sub>9</sub>] and (Me<sub>4</sub>N)[HgAs<sub>3</sub>S<sub>6</sub>],<sup>26</sup> (Me<sub>4</sub>N)[HgAsSe<sub>3</sub>], (Et<sub>4</sub>N)[HgAsSe<sub>3</sub>] and (Ph<sub>4</sub>P)<sub>2</sub>[Hg<sub>2</sub>As<sub>4</sub>Se<sub>11</sub>].<sup>27</sup> From the above instances we can see clearly that it is relatively rare for alkali metals cations used as structural directing agents to contain Hg/Cd arsenic chalcogenides in the M–TM–As–Q (M = alkali metals; TM = Hg, Cd; Q = S, Se) systems.<sup>8,28</sup> There is a common feature in the structures of these compounds, there are various degrees of condensation of the basic structural [AsQ<sub>3</sub>]<sup>3−</sup> (Q = S, Se) units through the chalcogen atoms as the ligands approach the transition metals.<sup>22,28,29</sup> Organic amines have been widely

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used in the solvothermal synthesis of quaternary transition metal chalcogenoarsenates owing to their structure directing effects. Our previous research has shown that  $\text{K}_2\text{CdSnS}_4$ ,<sup>30</sup>  $\text{Rb}_2\text{HgSnS}_4$ ,<sup>31</sup>  $\text{Cs}_8\text{Mn}_4\text{Sn}_4\text{Se}_{16}$ ,<sup>32</sup>  $\text{Cs}_2\text{HgSb}_4\text{S}_8$  and  $\text{Cs}_2\text{Hg}_2\text{Sb}_2\text{Se}_6$ ,<sup>3</sup> have different chains or layered structures, in contrast, ones that contain alkali-metal ions are still uncommon. In view of their significant potential to generate novel structures the transition metals Hg and Cd have been incorporated into the chalcogenoarsenates unit, to further the extend and investigate alkali metal ions as structural directing agents in chalcogenide systems. Recently, we have further expanded our work on solvothermal synthesis and synthesized four novel quaternary arsenic chalcogenides in the Cs-TM-As-Q system. In addition, we studied the properties of the four compounds.

## 2. Experimental section

### 2.1 Materials and methods

In this study, all of the chemical reagents used were of analytical grade, are commercially available and were used without further purification. The powder X-ray diffractometry (PXRD) was performed using a Rigaku XRD-6000 diffractometer using an operating power of 40 kV/40 mA and employing graphite-monochromatized Mo-K $\alpha$  radiation. The solid-state optical absorption spectra were recorded on a Shimadzu UV-2550 double monochromatic spectrophotometer over the range of 220–800 nm at room temperature using  $\text{Ba}_2\text{SO}_4$  power as the reflectance. The absorption spectrum data were calculated from the Kubelka–Munk function:  $\alpha/S = (1 - R)^2/2R$ , in which  $\alpha$  is the absorption coefficient,  $S$  the scattering coefficient, and  $R$  is the reflectance.<sup>42,43</sup> Differential scanning calorimetry (DSC) analyses were carried out using a STA 449 F5 Jupiter instrument under a nitrogen atmosphere (35 mL min<sup>-1</sup>) at 20–600 °C at a rate of 5 °C min<sup>-1</sup>.<sup>3</sup> The DSC data of compounds 1, 2 were obtained using a DSC-200F3 Maia instrument, compounds 3, 4 were obtained using a STA 449 F5 Jupiter instrument.

### 2.2 Synthesis of compounds 1–4

**Synthesis of  $\text{CsHgAsSe}_3$  (1).**  $\text{HgI}_2$  (12 mg, 0.026 mmol),  $\text{Cs}_2\text{CO}_3$  (15 mg, 0.046 mmol),  $\text{As}_2\text{S}_3$  (13 mg, 0.053 mmol) and Se (7 mg, 0.089 mmol) were placed into a Pyrex glass tube, and 1,4-dab (540 mg, 6.13 mmol) and  $\text{H}_2\text{O}$  (20 mg, 1.11 mmol) were added. The glass tube was sealed with a 10% filling, placed into a Teflon-lined stainless steel autoclave, and heated at 160 °C for 6 d. The products were washed with ethanol and water, respectively, and pure red crystals were obtained (17% yield). The crystals were washed with ethanol and dried and stored under vacuum.

**Synthesis of  $\text{CsCdAsSe}_3$  (2).** First,  $\text{Cs}_2\text{CO}_3$  (12 mg, 0.026 mmol),  $\text{As}_2\text{S}_3$  (14 mg, 0.057 mmol) and Se (7 mg, 0.089 mmol) were combined,  $\text{HgI}_2$  was replaced with  $\text{CdI}_2$  (11 mg, 0.030 mmol) and the reaction was performed in the same way as for (1), the mixture was heated to 150 °C for 6 d under the same mixed solvent. The other conditions remained unchanged to

obtain yellow block crystals of the compound  $\text{CsCdAsSe}_3$  (2) (19% yield).

**Synthesis of  $\text{Cs}_2\text{Cd}_2\text{As}_2\text{S}_6$  (3).** Yellow block crystals of the compound  $\text{Cs}_2\text{Cd}_2\text{As}_2\text{S}_6$  (3) were synthesized from  $\text{Cs}_2\text{CO}_3$  (17 mg, 0.052 mmol),  $\text{As}_2\text{S}_3$  (12 mg, 0.05 mmol),  $\text{CdI}_2$  (19 mg, 0.051 mmol) and S (6 mg, 0.2 mmol) in 1,2-dap (531 mg, 6.91 mmol) and  $\text{H}_2\text{O}$  (12 mg, 6.89 mmol), the reaction was heated at 140 °C for 7 d to obtain compound 3 (20% yield).

**Synthesis of  $\text{Cs}_2\text{Hg}_2\text{As}_2\text{S}_6$  (4).**  $\text{Cs}_2\text{Hg}_2\text{As}_2\text{S}_6$  (4) was synthesized using the same method as that used for compounds 1–3, the majority of conditions remained unchanged, in 1,2-dap (512 mg, 6.91 mmol) and  $\text{H}_2\text{O}$  (17 mg, 6.89 mmol),  $\text{Cs}_2\text{CO}_3$  (17 mg, 0.052 mmol),  $\text{As}_2\text{S}_3$  (12 mg, 0.05 mmol) and S (7 mg, 0.022 mmol) were combined,  $\text{CdI}_2$  was used instead of  $\text{HgI}_2$  (22 mg, 0.049 mmol) to obtain yellow block crystals of compound  $\text{Cs}_2\text{Hg}_2\text{As}_2\text{S}_6$  (4) (22% yield).

### 2.3 Single-crystal X-ray diffraction

The PXRD patterns of 1–4 are shown in Fig. S3.† The  $2\theta$  values for all peaks exhibit a good match with the corresponding simulated results from the single-crystal diffraction data, indicating the high purity of all of the above-mentioned samples. Polycrystalline samples of the title compounds of 1–4 with dimensions of 0.23 × 0.20 × 0.14 mm, 0.26 × 0.21 × 0.19 mm, 0.28 × 0.25 × 0.22 mm and 0.28 × 0.25 × 0.20 mm were collected with the crystal diffraction intensity data on a Bruker APEX-II CCD diffractometer equipped with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296 K. The structures of 1–4 were solved using direct methods and refined using full-matrix least-square methods on  $F^2$  by the SHELXL 97 package.<sup>43,44</sup> The related crystallographic data and structural refinement parameters for the 1–4 compounds are summarized in Table S1,† and some part relevant bond distances and bond angles at listed in Tables S2–S5 (ESI).†

## 3. Results and discussion

### 3.1 Synthetic considerations

The formation of crystals is affected by the different proportions of the initial reactant. The described synthesis methods were found to be the most effective to yield the title compounds and the reproducibility of all the products was good. In compound 1,  $\text{HgI}_2$  was replaced with  $\text{CdI}_2$  powder to obtain 2, other salts were formed that contained mercury but did not form crystals. No target crystals were obtained in repeated experiments in which the Se powder was replaced with S powder. For compound 3, when Cd powder was used instead of  $\text{CdI}_2$  as the reactant, a small number of crystals were found, but there were more black impurities, which may be because  $\text{Cd}^{2+}$  had a stronger reactivity than Cd. For 4, other mercury-containing salts and a small number of crystals were formed, with further impurities and a low yield. In addition, in the solvent system for the synthesis of these four compounds, attempts were made to replace  $\text{HgI}_2$  or  $\text{CdI}_2$  with salts containing other transition metal ions, and no crystal formation was observed. When other carbonates of alkali metals were used instead of  $\text{Cs}_2\text{CO}_3$  as reactants, it was found



that no crystals were formed, as the size of the counter ion radius has a significant influence on the synthesis. Meanwhile, the counter ion may play a certain role in the stability of the anionic skeleton. For **1** and **2**, the use of other organic solvents, instead of 1,4-dab, did not result in crystals. For compounds **3** and **4**, if 1,4-dab or ethanediamine were used instead of 1, 2-dap as the reaction solvent, no crystals were formed. In conclusion, in the synthetic environment of compounds **3** and **4**, 1,2-dap is more suitable for the synthesis of compounds **3** and **4** than the other organic solvents. If the reaction solvent used for compounds **1–4** is not added with water, the synthesized crystals are all gathered together, therefore water may increase the solubility of the reactants during the reaction.

### 3.2 Structural descriptions

The crystal data for compounds **1–4** and their related parameters are shown in Table S1 (ESI<sup>†</sup>), and the structure of CsHgAsSe<sub>3</sub> (**1**) shown using single-crystal X-ray diffraction analysis<sup>23</sup> reveals that **1** crystallizes in the monoclinic space group *P*<sub>21</sub>/*n*. It is isostructural with (Me<sub>4</sub>N)[HgAsSe<sub>3</sub>] and (Et<sub>4</sub>N)[HgAsSe<sub>3</sub>].<sup>27</sup> The compound contains one-dimensional chains consisting of trigonal-planar Hg<sup>2+</sup> ions and [AsSe<sub>3</sub>]<sup>3-</sup> units. The [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> chains are parallel to the crystallographic *a* axis and separated by Cs<sup>+</sup> cations (Fig. S1, ESI<sup>†</sup>).

For **1**, the alternating connection of the two trigonal planar [HgSe<sub>3</sub>] and two trigonal pyramids [AsSe<sub>3</sub>] (Fig. 1a) gives rise to a heterometallic 8-membered [Hg<sub>2</sub>As<sub>2</sub>Se<sub>6</sub>] ring (Fig. 1b), which further connects with the neighbouring 8-membered rings and forms a [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> anion chain by edge-sharing (Hg1–Se2–As1) (Fig. 1c) the two coordination Se as a bridge using As and Hg. The common [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> 1D anion chain of compound **1** is similar to that observed in (R<sub>4</sub>N)[HgAsSe<sub>3</sub>] (R = Me, Et).<sup>26</sup> Both structures contain the Hg<sub>2</sub>As<sub>2</sub>Q<sub>4</sub> 8-membered rings, but the counterions are different. The relationship lies in the fact that the structural motif in the [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> can be derived from that of [Hg<sub>2</sub>As<sub>2</sub>Q<sub>4</sub>]<sub>*n*</sub><sup>*2n-*</sup> by substitution of one fourth of the arsenic atoms for Hg.<sup>27</sup> As above, a similar chain consists of heterometallic 8-membered rings, such as the infinite anionic [In<sub>2</sub>Sb<sub>2</sub>S<sub>8</sub>]<sub>*n*</sub><sup>*4n-*</sup> chain by two [InS<sub>4</sub>] and two [SbS<sub>3</sub>] units, which joined to yield an 8-membered [In<sub>2</sub>Sb<sub>2</sub>S<sub>4</sub>] ring in a chair-like conformation, which is further interconnected at the In atom.<sup>33</sup> In compounds K<sub>2</sub>MSb<sub>3</sub>(SH) (M = Zn, Cd), each of the

[M<sub>2</sub>Sb<sub>2</sub>S<sub>8</sub>(SH)<sub>2</sub>]<sub>*n*</sub><sup>*8-*</sup> eight-membered rings is formed by two [MS<sub>3</sub>(SH)]<sup>5-</sup> tetrahedra and two [SbS<sub>3</sub>]<sup>3-</sup> pyramids by corner sharing, the eight-membered rings with an opposite orientation are further connected to form an eight-membered ring 1-D chain.<sup>34</sup>

The [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> anion contains three crystallographically distinct Se atoms, one Hg atom and one As atom. The Hg<sup>2+</sup> is in the trigonal-planar environment with bond angles of Se1–Hg1–Se3 at 120.24(6)°, Se1–Hg1–Se2 at 121.95(5)°, and Se3–Hg1–Se2 at 117.41(6)° (Table S2<sup>†</sup>). The Hg–Se distances are in the range of 2.571(2)–2.592(2) Å, and the Hg–Se bond lengths match well with those observed in the HgSe<sub>3</sub> trigonal-planar of (Me<sub>4</sub>N)[HgAsSe<sub>3</sub>] and (Et<sub>4</sub>N)[HgAsSe<sub>3</sub>] (Hg–Se: 2.572(2)–2.594(1) Å).<sup>27</sup> All As atoms are coordinated by three Se atoms at distances in the range of 2.372(2)–2.404(2) Å, with Se–As–Se angles in the range of 97.94(7)–101.20(7), forming typical trigonal pyramidal AsSe<sub>3</sub> units. The bond lengths and angles of the AsSe<sub>3</sub> units are consistent with the corresponding values reported in selenoarsenate compounds.<sup>21,26</sup> All selenium atoms join an As and a Hg atom with As–Se–Hg angles in the range of 90.48(8)–93.31(7)° (Table S2<sup>†</sup>).

Apparently, the different coordination modes of the Hg atom, to some extent, affect their roles in constructing the structures. In addition, when the Hg atoms in compound **1** are replaced with Cd atoms, they undergo interesting structural changes, an eight-membered ring chain structure similar to that found in compound **1** is further connected by Cd–Se to form a layered structural compound CsCdAsSe<sub>3</sub> (**2**) (Fig S2, ESI<sup>†</sup>).

The [CdAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> anion contains three crystallographically distinct Se atoms, one Cd atom and one As atom. The As atom is in the same coordinated form as in compound **1**, the distances are in the range of 2.351(4)–2.406(4) Å, with Se–As–Se angles in the range of 98.58(14)–102.00(14) (Table S3<sup>†</sup>), the bond lengths and angles of the AsSe<sub>3</sub> units are consistent with the corresponding values reported in selenoarsenate compounds.<sup>23</sup> The Cd atom is coordinated by four Se atoms at distances in the range of 2.597(4)–2.719(4) Å, forming a significantly distorted CdSe<sub>4</sub> tetrahedron with Se–Cd–Se angles in the range of 94.58(11)–122.96(12) (Table S3<sup>†</sup>). Except for Se(3), which is coordinated by two Cd and an As atom, with Cd–Se–As(Cd) angles in the range of 97.14(12)–115.22(11)°, the remaining two crystallographically independent selenium atoms join the As and a Cd atoms to form As–Se–Cd angles in the range of 88.34(12)–95.55(12)° (Table S3<sup>†</sup>). Considering the diversity of the transition metal–selenium bonding, the introduction of different transition metal can lead to different ways of bridging the selenoanionic species, consequently producing a variety of structures. This result shows that the cadmium ions in **2** play a key role in the formation of the layers. The [CdAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> anion chain forms a 2D layered structure, which consists of rings similar to the heterometallic 8-membered rings that form the [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> chains in compound **1**. Similarly structural eight-membered rings of the Cd<sub>2</sub>As<sub>2</sub>Se<sub>6</sub> units were also observed in (Me<sub>4</sub>N)[HgAs<sub>3</sub>Se<sub>6</sub>],<sup>27</sup> C<sub>20</sub>H<sub>80</sub>In<sub>6</sub>N<sub>20</sub>Ni<sub>3</sub>S<sub>21</sub>Sb<sub>6</sub>,<sup>33</sup> KAgAsS<sub>2</sub>,<sup>35</sup> Cs<sub>2</sub>Hg<sub>3</sub>M<sub>2</sub>S<sub>8</sub> (M = Sn, Ge),<sup>36</sup> [1,2-pdaH]HgSbS<sub>3</sub> and [Ni(en)<sub>3</sub>]<sub>0.5</sub>HgSbS<sub>3</sub>,<sup>37</sup> but the

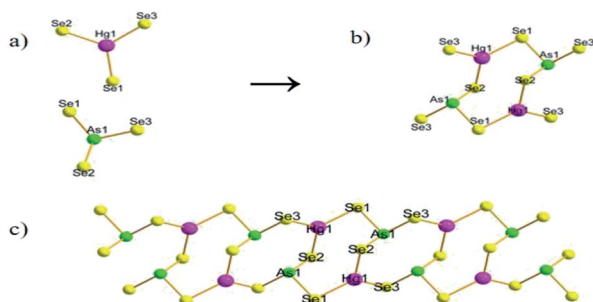


Fig. 1 (a) The [HgSe<sub>3</sub>] unit and [AsSe<sub>3</sub>] unit. (b) The 8-membered [Hg<sub>2</sub>As<sub>2</sub>Se<sub>6</sub>] ring. (c) The structure of the [HgAsSe<sub>3</sub>]<sub>*n*</sub><sup>*n-*</sup> anion chain in **1**.



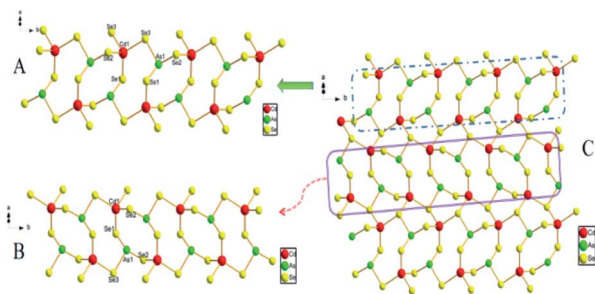


Fig. 2 The opposite orientation  $[\text{CdAsSe}_3]_n^{n-}$  chains in A/B formation in the 2D network C for compound 2.

connections were different. For example, the 2D  $[\text{Hg}_3\text{M}_2\text{S}_8]^{2-}$  layer is formed by the two coordinated Hg atom between the chains of alternating eight-membered ring chains in  $\text{Cs}_2\text{Hg}_3\text{M}_2\text{S}_8$  ( $\text{M} = \text{Sn}, \text{Ge}$ ).<sup>36</sup> The oppositely orientated adjacent  $[\text{CdAsSe}_3]_n^{n-}$  chains A/B connect with each other *via* Cd1–Se3 bonds to form a 2D network C (Fig. 2). Simultaneously, 6-membered rings of  $[\text{Cd}_2\text{AsSe}_3]$  can arise between the 8-membered ring chains. Similar heterometallic 6-membered rings to those described above were also observed in  $\text{NaAg}_2\text{AsS}_3 \cdot \text{H}_2\text{O}$  and  $\text{KAg}_2\text{AsS}_3$ .<sup>12</sup>  $\text{KCu}_2\text{SbS}_3$ ,<sup>38</sup> in the compound  $\text{KCu}_2\text{SbS}_6$ , are six-membered hetero rings  $[\text{Cu}_2\text{SbS}_3]$  that edge-share to form a single layer, these layers are combined together by Cu(3)–S and Cu(4)–S that form a 2D double-layered structure,<sup>38</sup> the compound  $\text{KCu}_2\text{SbS}_3$  is composed of distorted 6-membered  $\text{Cu}_2\text{SbS}_3$  rings attached *via* edge sharing to form  $[\text{Cu}_2\text{SbS}_3]$  hexagonal nets.<sup>39</sup> As far as we know, only the compounds  $\text{RbCu}_4\text{AsS}_4$ ,<sup>35</sup>  $(1,4\text{-DABH}_2)\text{Cd}_2\text{Sb}_2\text{S}_6$ ,<sup>40</sup> and  $[\text{enH}_2]_{0.5}[\text{HgSbS}_3]$  (ref. 37) have 8-membered rings and 6-membered rings, but the connections and the structure of the connection in compound 2 are different. The structural difference between them indicates that amine, alkali and alkaline earth metals have different structure-directing effects on the crystallization of the arsenic chalcogenides. The transition metals also have structure directing roles in quaternary

chalcogenides, although they differ from that of alkali-, alkaline earth and amines in the synthesis of chalcogenides.<sup>41</sup>

Therefore, further understanding of the role of the structural directing agent will be important for the rational design and synthesis of novel chalcogenides. The ternary Cd–As–Q frameworks are rare compared with a variety of Hg–As–Q, Cu–As–Q and Ag–As–Q networks.  $\text{CsCdAsSe}_3$  (2) is the only example of the cadmium selenoarsenates that contain the charge-balancing ions of cesium cations. To the best of our knowledge, this type of layer was never reported in the M–As–Q compounds. The formation of 1 and 2 indicates that the  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  ions are respectively incorporated into the 1D and 2D selenoarsenate(III) networks. If the 1,4-diaminobutane is replaced with 1,2-diaminopropane, two new compounds are formed,  $\text{Cs}_2\text{M}_2\text{As}_2\text{S}_6$  ( $\text{M} = \text{Cd}$  (3), Hg (4)). The Cd and Hg atoms are four coordinated. Single-crystal X-ray diffraction analysis<sup>22</sup> reveals that 3 and 4 are isostructural, and like 2 they crystallize in the monoclinic space group  $P_{21/n}$ .

To the best of our knowledge, different structural chalcogenides with similar chemical compositions to  $\{\text{Hg}/\text{Cd}-\text{Sb}/\text{As}-\text{Q}_3\}$  have been reported, but synthesis of the common eight-membered ring structures by different structural directing agent, including  $(\text{R}_4\text{N})[\text{HgAsSe}_3]$  ( $\text{R} = \text{Me}, \text{Et}$ ),<sup>27</sup>  $(\text{Ph}_4\text{P})_2[\text{Hg}_2\text{As}_4\text{S}_9]$ ,<sup>26</sup>  $(\text{RH}_2)_{0.5}[\text{HgSbS}_3]$  ( $\text{R} = \text{en}, \text{teta}$ ) has not previously been reported.<sup>37</sup> The layers of compounds 2–4 were similar to  $(\text{RH}_2)_{0.5}[\text{HgSbS}_3]$  ( $\text{R} = \text{en}, \text{teta}$ ), although they are all composed of six-membered  $\text{Hg}(\text{Cd})_2\text{-As}(\text{Sb})/\text{Q}_3$  ( $\text{Q} = \text{S}, \text{Se}$ ) rings and eight-membered  $\text{Hg}(\text{Cd})_2\text{-As}(\text{Sb})_2/\text{Q}_4$  rings, the arrangement of the two types of rings are quite different.

### 3.3 Thermogravimetric and differential scanning calorimetry analyses

The DSC data for compounds 1, 2 were obtained under an Ar atmosphere, the data for compounds 3, 4 were obtained under an  $\text{N}_2$  atmosphere from 20–530 °C and 25–600 °C (Fig. S4†). The data shows the DSC curves of compounds 1–4 display endothermic peaks at 429.9, 429.9, 452 and 357 °C respectively. The main reason for this is that the structure of compounds 1–4 collapses at different temperature (Fig. S4, ESI†).<sup>29</sup>

### 3.4 Optical properties

The UV-vis reflectance spectroscopy of the powder samples of compounds 1–4 was recorded at room temperature. The solid-state optical absorption data for compounds 1–4 are shown in Fig. 3. The absorption data indicates that the optical band gaps are 1.91 eV for 1, 2.12 eV for 2, 2.71 eV for 3 and 2.58 eV for 4, respectively, as calculated from the reflectance data using the Kubelka–Munk function. The band gaps for compounds 1–4 are similar to the selenidoarsenates and thioantimonates  $\text{Cs}_3\text{AgAs}_4\text{Se}_8$  (2.10 eV),  $\text{CsAgAs}_2\text{Se}_4$  (1.79 eV),<sup>15</sup>  $(\text{R}_4\text{N})[\text{HgAsSe}_3]$  ( $\text{R} = \text{Me}, \text{Et}$ ) (2.4 eV),<sup>27</sup>  $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{Se}_5$  (2.67 eV),<sup>45</sup>  $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{S}_5$  (2.71 eV),<sup>43</sup>  $\text{Cs}_2\text{AgAsS}_4$  (2.7 eV),<sup>46</sup>  $\text{RbCu}_2\text{As}^{\text{III}}\text{S}_3$  (1.96 eV),  $\text{RbCu}_4\text{As}^{\text{III}}\text{S}_4$  (2.15 eV),<sup>35</sup>  $\text{CsCu}_2\text{AsS}_3$  (2.3 eV),<sup>41</sup> and  $\text{CsAg}_2\text{AsS}_3$  (2.7 eV),<sup>47</sup> all of which have semiconductor properties.

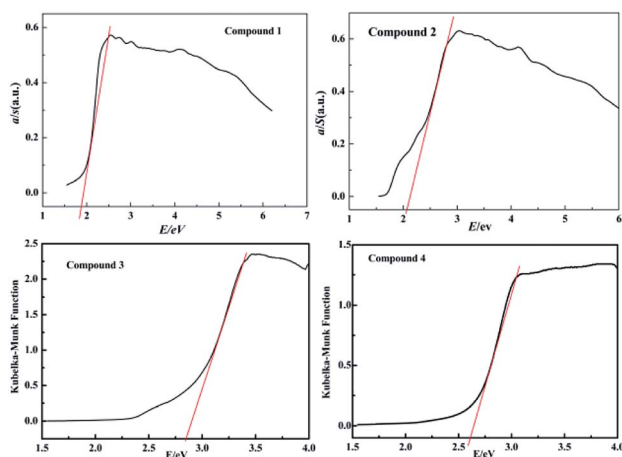


Fig. 3 Solid-state optical absorption spectra for compounds 1–4.



## 4. Conclusions

In this work, we have successfully prepared quaternary chalcogenides and synthesized four novel compounds in the Cs-TM-As-Q system using a solvothermal method. The solid-state optical absorption spectra indicate that the four compounds are semiconductors. Although the four compounds have similar chemical compositions and the same proportions, their structures and transition metal ion coordination modes are different from each other. It can be seen that different organic solvents, used as mineralizers, and solvothermal methods can be used to synthesize arsenic chalcogenides containing mercury or cadmium, Hg/Cd-As-Q (Q = S, Se), connected in various modes and result in Hg/Cd arsenic chalcogenides with architectures that range from 1D chains to 2D layers. The chain lengths of the different bidentate organic amines are different and their roles in selenides and sulfides are different. This not only enriches the structural chemistry, but also provides novel method for the synthesis of arsenic chalcogenides. This could be used to investigate which properties have significance for the synthesis of arsenic chalcogenides containing different transition metal elements in an anionic framework.

## Conflicts of interest

There are no conflicts to declare.

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