Electronic Supplementary Information (ESI)

A novel bifunctional thioarsenate based on unprecedented molecular [Cd$_4$As$_8$Se$_{16}$(Se$_2$)$_2$]$^{8-}$ cluster anions

Xin Chen,‡[a] Sheng-Hua Zhou,‡[b,c,d] Chao Zhang,[a] Hua Lin,[*,b,c] and Yi Liu[*,a]

[a]*Institute for Composites Science Innovation (InCSI), School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

[b]*Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou 350108, China*

[c]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

[d]*University of Chinese Academy of Sciences, Beijing 100049, China*

‡X. Chen and S. H. Zhou contributed equally to this work

*E-mail: liuyimse@zju.edu.cn and linhua@fjirsm.ac.cn.

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1. Experimental Section

Physical Measurements. The elemental analyses have been examined with via an EDX-equipped JEOL/JSM-6360A SEM. Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer with a graphite-monochro-matized Cu K_α radiation. The operating 2θ angle ranges from 10° to 70°. Simulation of XRD patterns were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 1.4.2 available free of charge through the website http://www.iucr.org. The optical diffuse reflectance spectra were measured on a Hitachi UH4150 UV–vis-NIR spectrometer equipped with an integrating sphere at room temperature. The picked polycrystalline samples were ground into fine powders before measurement. The absorption (α/S) data were calculated from reflectance with the Kubelka–Munk function: $\alpha/S = (1–R)^2/2R$, in which α is the absorption coefficient, R is the reflectance at a specified wavelength, and S is the scattering coefficient.[1] The photo-electrochemical tests were done under simulated solar light illumination using an electrochemical workstation (CHI660E) with conventional three-electrode setup on open circuit voltage. Each as-prepared powder sample was coated onto a slice of ITO glass with an area of 0.5×1 cm^2 and employed as the working electrode. A saturated Hg/Hg_2Cl_2 and a platinum wire were used as the reference and counter electrodes, respectively, and 0.2 M Na_2SO_4 aqueous solution with 10% lactic acid was used as electrolyte. A 500 W Xe lamp was utilized as the simulated solar light source.

Syntheses of Cs$_2$CdAsSe$_5$. The starting reagents CsOH·H$_2$O (99.7%), Cd powder (99.99%) and PEG-400(99.5%) purchased from Sinopharm Chemical

Reagent Co., Ltd. 1,2-Propanediamine (99%), Cd powder (99.99%) and the binary starting material As_2Se_3 (99.9%) was purchased from Aladdin Co., Ltd. All the chemicals used for synthesis are of analytical grade and directly used without further purification.

Compound $Cs_2CdAsSe_5$ was obtained by the reaction as follows: 1 mmol of $CsOH \cdot H_2O$, 0.6 mmol of Cd, 0.5 mmol of As_2Se_3, 2.5 mmol of Se, 2 mL of PEG-400 and 1 mL of 1,2-Propanediamine. All reactants were sealed in a 25 mL Teflon-lined stainless autoclave which was kept at 453 K for 7 days prior to cooling to room temperature naturally. The resultant reaction mixtures were washed with distilled water and ethanol, respectively. A lot of purple block-shaped $Cs_2CdAsSe_5$ crystals (approximately 70% yield based on Cd) were obtained and pure phase could be easily obtained by manually picking crystals from the mixtures.

Single-Crystal Structure Characterizations. Suitable single crystals of the title compounds were mounted on the glass fibers. Diffraction data were collected by an Oxford Xcalibur (Atlas Gemini ultra) diffractometer with a graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at room temperature. The absorption corrections were based on the multi-scan method. The structures were solved by the direct methods and refined by the full-matrix least-squares fitting on F^2 using the *SHELXL-2014* software package.[2] The assignments of atoms were determined on the basis of the interatomic distances, coordination environments and relative displacement parameters. The structure was verified using the *ADDSYM* algorithm from the program *PLATON*.[3] The final atomic positions were standardized with the

STRUCTURE TIDY program.[4] Crystal data and refinement details are summarized in Tables 1-2, the selected bond lengths are listed in Table S3. CCDC number: 2215340.

Computational Details. Crystallographic data determined by single crystal X-ray diffraction were used for theoretical calculations of their electronic band structures. The density functional theory (DFT) calculations have been performed using the Vienna ab initio simulation package (VASP)[5-7] with the Perdew-Burke-Ernzerhof (PBE)[8] exchange correlation functional. The projected augmented wave (PAW)[9] potentials have been used to treat the ion-electron interactions. A Γ-centered $5\times5\times7$ Monkhorst-Pack grid for the Brillouin zone sampling and a cutoff energy of 700 eV for the plane wave expansion were found to get convergent lattice parameters and self-consistent energies.
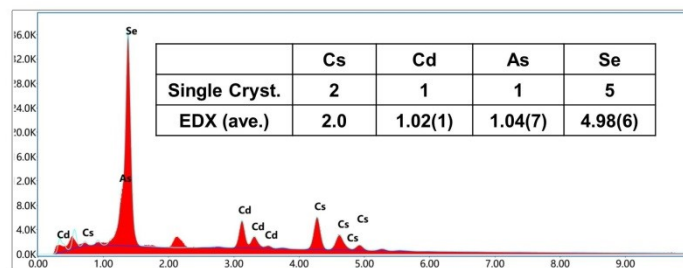
Figures and Tables

Figure S1. Energy-dispersive X-ray spectroscopy analysis of $Cs_2CdAsSe_5$.

Table S1. Crystallographic data and refinement details for $Cs_2CdAsSe_5$.

formula	$Cs_2CdAsSe_5$
fw	847.94
crystal system	Tetragonal
Temperature (K)	453
crystal colour	purple
space group	$P4_2/n$ (no. 85)
a (Å)	17.9368(6)
b (Å)	17.9368(6)
c (Å)	7.5125(4)
α (deg.)	90
β (deg.)	90
γ (deg.)	90
V (Å^3)	2417.0(2)
Z	8
D_c (g/cm^3)	4.660
μ (mm^{-1})	25.456
GOOF on F^2	1.067
refines/parameters/restraints	2119/83/0
R_1, wR_2 (I > 2σ(I))[a]	0.0461, 0.1150
R_1, wR_2 (all data)	0.0481, 0.1160
largest diff. Peak / hole (e/Å^3)	2.018/-1.323

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters of $Cs_2CdAsSe_5$.

Atom	*Wyckoff*	*x*	*y*	*z*	$U_{(eq)}$*	*Occu.*
Cs1	8g	0.65814(7)	0.13587(7)	0.2663(2)	0.0437(4)	1.0
Cs2	8g	0.39624(5)	0.07806(5)	0.23434(12)	0.0205(2)	1.0
Cd	8g	0.37872(6)	0.30865(6)	0.77950(14)	0.0176(3)	1.0
As	8g	0.34227(8)	0.51564(8)	0.7614(2)	0.0153(3)	1.0
Se1	8g	0.12187(9)	0.86336(8)	0.7203(2)	0.0270(4)	1.0
Se2	8g	0.47786(9)	0.23241(8)	0.9761(2)	0.0206(3)	1.0
Se3	8g	0.00029(8)	0.72400(8)	0.5192(2)	0.0201(3)	1.0
Se4	8g	0.43882(8)	0.05223(8)	0.7417(2)	0.0188(3)	1.0
Se5	8g	0.23988(8)	0.18306(8)	0.99952(19)	0.0155(3)	1.0

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond lengths (Å) for $Cs_2CdAsSe_5$.

As–Se1	2.2846(17)	Cs1–Se1	3.683(2)	Cs2–Se1	3.6360(16)
As–Se2	2.3315(17)	Cs1–Se1	3.885(2)	Cs2–Se2	3.6849(15)
As–Se3	2.2879(18)	Cs1–Se1	3.9469(18)	Cs2–Se2	3.7906(15)
As–Se4	2.3426(17)	Cs1–Se1	4.1325(17)	Cs2–Se3	3.7109(15)
Cd–Se2	2.6852(16)	Cs1–Se2	4.2670(17)	Cs2–Se3	3.7592(15)
Cd–Se4	2.6475(15)	Cs1–Se2	3.7913(18)	Cs2–Se4	3.8065(16)
Cd–Se5	2.6726(15)	Cs1–Se3	3.8700(17)	Cs2–Se4	3.9154(16)
Cd–Se5	2.6975(15)	Cs1–Se3	3.6209(16)	Cs2–Se5	3.8008(14)
		Cs1–Se4	3.7962(17)	Cs2–Se5	3.8110(14)

Table S4. Structural features of selected chalcogenides in the $X-M-As^V-Q$ (X = charge-balanced cations; M = metal elements; Q = chalcogen) system.

Structure type	Compounds	Crystal system	Space group	Structural dimension	Ref.
1–1–1–4	$SrAgAsS_4$	orthorhombic	*Ama*2 (no. 40)	2D	10
	$NaEuAsS_4$	orthorhombic	*Ama*2 (no. 40)	3D	11
	$KEuAsS_4$	monoclinic	$P2_1/m$ (no.11)	2D	12
1–2–1–4	KAg_2AsS_4	tetragonal	*I-42m* (no.121)	3D	13
	$RbAg_2AsS_4$	triclinic	$P\bar{1}$ (no.2)	1D	14
	$(NH_4)Ag_2AsS_4$	tetragonal	$I\bar{4}2m$ (no.121)	3D	15
2–1–1–4	Cs_2AgAsS_4	triclinic	$P\bar{1}$ (no.2)	1D	16
	K_2AuAsS_4	monoclinic	$P2_1/m$ (no.11)	1D	17
2–1–1–5	Cs_2CdAsS_5	tetragonal	$P4_2/n$ (no. 86)	0D	This work
3–1–2–8	$Cs_3BiAs_2S_8$	monoclinic	$P2_1/m$ (no.11)	1D	18
	$K_3SmAs_2S_8$	monoclinic	*C2/c* (no.15)	1D	19
	$K_3GdAs_2S_8$	monoclinic	*C2/c* (no.15)	1D	19
	$K_3TbAs_2S_8$	monoclinic	*C2/c* (no.15)	1D	19
	$K_3DyAs_2S_8$	monoclinic	*C2/c* (no.15)	1D	12
4–1–2–8	$K_4MnAs_2S_8$	monoclinic	*P2/c* (no.13)	0D	20
	$Rb_4MnAs_2S_8$	triclinic	$P\bar{1}$ (no.2)	0D	20
	$Cs_4MnAs_2S_8$	triclinic	$P\bar{1}$ (no.2)	0D	20
4–1–2–9	$Rb_4CdAs_2S_9$	triclinic	$P\bar{1}$ (no.2)	0D	20
4–1–2–10	$Ba_4HgAs_2S_{10}$	monoclinic	*C2/c* (no.15)	0D	21
5–16–7–28	$(NH_4)_5Ag_{16}As_7S_{28}$	monoclinic	*C/c* (no. 9)	3D	22
7–4–3–13	$Rb_7Cu_4As_3S_{13}$	trigonal	*P31c* (no.159)	0D	23
	$Cs_7Cu_4As_3S_{13}$	trigonal	$P\bar{3}$ (no.147)	0D	23

4. References

[1] G. Kortüm, *Reflectance Spectroscopy*; Springer-Verlag: NewYork, 1969.

[2] Sheldrick, G. M. A short history of SHELX, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2008, 112–122.

[3] A. L. Spek, Single-crystal structure validation with the program PLATON, *J. Appl. Cryst.,* 2003, **36**, 7–13.

[4] L. M. Gelato and E. *J.* Parthe, STRUCTURE TIDY–a computer program to standardize crystal structure data, *Appl. Crystallogr.,* 1987, **20**, 139–143.

[5] G. Kresse, VASP, 5.3.5; http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html.

[6] G. Kresse and J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B: Condens. Matter,* 1996, **54**, 11169–11186.

[7] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B: Condens. Matter,* 1999, **59**, 1758–1775.

[8] J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.,* 1996, **77**, 3865–3868.

[9] P. E. Blochl, Projector augmented-wave method, *Phys. Rev. B: Condens. Matter,* 1994, **50**, 17953–17979.

[10] J. Tang, F. Liang, C. Tang, W. Xing, J. Wu, W. Yin, B. Kang and J. Deng, *Inorg. Chem.*, 2022, **61**, 9205–9212.

[11] T. K. Bera and M. G. Kanatzidis, *Inorg. Chem.*, 2012, **51**, 4293–4299.

[12] Y. D. Wu and W. Bensch, *Solid State Sci.*, 2009, **11**, 1542–1548.

[13] G. L. Schimek and J. W. Kolis, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 991–992.

[14] Y. Li, X. Song, Y. Zhong, Y. Guo, M. Ji, Z. You and Y. An, *J. Alloys Compd.*, 2021, **872**, 159591.

[15] M. Auernhammer, H. Effenberger, E. M. Irran, F. Pertlik and J. Rosenstingl, *J. Solid State Chem.*, 1993, **106**, 421–426.

[16]   P. T. Wood, G. L. Schimek and J. W. Kolis, *Chem. Mater.*, 1996, **8**, 721–726.

[17]S. Loeken and W. Tremel, *Eur. J. Inorg. Chem.*, 1998, **1998**, 283–289.

[18] T. K. Bera, R. G. Iyer, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.*, 2013, **52**, 11370–11376.

[19] Y. Wu, C. Naether and W. Bensch, *Inorg. Chem.*, 2006, **45**, 8835–8837.

[20] P. N. Iyer and M.G. Kanatzidis, *Inorg. Chem.*, 2004, **43**, 3656–3662.

[21] W. Xing, N. Wang, Z. Li, W. Liu, J. Tang, W. Yin, Z. Lin, B. Kang and J. Yao *Dalton Trans.*, 2020, **49**, 13060–13065.

[22] F. Pertlik, *Monatsh. Chem.*, 1994, **125**, 1311–1319.

[23] Y. Li, X. Cao, M. Ji, Z. You and Y. An, *Inorg. Chem. Commun.*, 2022, **139**, 109365.