

$[\text{Zn}(\text{H}_2\text{O})_4][\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$: a robust open framework chalcogenide with a large nonlinear optical response†

Manolis J. Manos,^a Joon I. Jang,^b John B. Ketterson^b and Mercuri G. Kanatzidis^{*a}

Received (in Berkeley, CA, USA) 17th August 2007, Accepted 28th November 2007

First published as an Advance Article on the web 18th December 2007

DOI: 10.1039/b712732d

$[\text{Zn}(\text{H}_2\text{O})_4][\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$ has an open polar framework based on supertetrahedral clusters with a unique double connectivity mode and exhibits a strong second harmonic generation response, excellent acid stability and proton exchange capacity.

Open framework chalcogenides are becoming increasingly appealing for a broadening set of applications.^{1–9} Their potential semiconducting properties and the presence of heavier chalcogen atoms impart to them physical and chemical attributes that are lacking in most other open frameworks (such as zeolites¹⁰ and metal–organic frameworks¹¹). These include optical-photonic phenomena,^{4a,c} fast ionic conductivity,^{4b}

solar hydrogen generation^{4e} and heavy metal remediation.^{2f,9}

For the chalcogenide family, considerable work has been reported on group 13 and/or 14 based systems such as indium^{2f,3c,5} and tin⁸ sulfides/selenides. On the other hand, combining different metal ions can diversify the chemistry and is attractive as a strategy for obtaining acentric arrangements due to the simultaneous presence of two kinds of metal center with different sizes, coordination preferences and packing characteristics.¹² Indeed, a number of hetero-bimetallic open framework chalcogenides with non-centrosymmetric structures have been reported.^{2b–e,4d,7b}

We describe here a novel 3D open framework chalcogenide $[\text{Zn}(\text{H}_2\text{O})_4][\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$ (**1**) employing hydrothermal synthesis techniques in highly concentrated amine.† Compound (**1**) is templated by a metal hydrate and exhibits exceptional stability under extremely acidic conditions, a property which allowed the isolation of the solid acid analogue of this material. The unique polar structure creates a strong nonlinear optical response and second harmonic generation (SHG). Although the number of non-centrosymmetric open framework chalcogenides has been increasing, very few reports exist on nonlinear optical (NLO) studies of such materials.

Herein, we give one of the first reports on the NLO properties of such compounds.

Compound **1** crystallizes in the triclinic space group $P1\bar{1}$. The critical building unit of **1** is the $[\text{ZnSn}_3\text{Se}_{10}]^{6-}$ cluster (**1a**), which features a T2¹³ supertetrahedron (Fig. 1). To the best of our knowledge, no T2 chalcogenide cluster with tin and zinc centres has been reported prior to this work. By sharing Se atom corners, the **1a** clusters are connected to each other along the *a*-axis forming chains [Fig. 1(a)]. To form the 3D framework, the chains are interconnected, along the directions of the *b* and *c*-axes, through zinc (Zn_2) metal linkers [Fig. 1(b)]. Unlike most other open framework chalcogenides constructed by linking four clusters through a metal centre, each Zn_2 atom in **1** is connected with three clusters, with the fourth coordination site of Zn_2 occupied by a terminal methylamine ligand.¹⁴ The double connectivity mode of T2 clusters of **1** (by sharing corners and through a metal linker) is a new binding mode among open framework chalcogenides.

The existence of a neutral ligand such as methylamine on a Zn^{2+} center which is part of the 3D framework is a rare and interesting finding. It suggests that, under appropriate circumstances, MeNH_2 could be a facile leaving group to generate coordination unsaturation on the Zn^{2+} center making it a stronger Lewis acid useful in catalysis.

Another noticeable structural feature of **1** is the presence of $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ aqua complexes in the pores of the framework [Fig. 1(b)] acting as counter cations and a structure-directing agent.¹⁵ The Zn atom of this cation adopts a slightly distorted tetrahedral geometry. The O–Zn–O bond angles [107.1(5)–111.8(5)°] and the Zn–OH₂ distances [2.019(12)–2.059(10) Å] are in good agreement with those reported in the literature for $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ complexes.¹⁵

At this point, it is worth comparing the structure of **1** with that of the recently reported chalcogenide $[\text{Zn}(\text{C}_6\text{N}_4\text{H}_{18})(\text{H}_2\text{O})][\text{Ge}_3\text{S}_6\text{Zn}(\text{H}_2\text{O})\text{S}_3\text{Zn}(\text{H}_2\text{O})]$ (**2**) which also contains a Zn metal centre linking three T2 clusters and a metal complex as a structure-directing agent.^{4d} There are distinctive differences between the structures of **1** and **2**: (a) compound **1** is 3D, while compound **2** is layered and (b) the T2 clusters of **1** are connected with two different modes (see above), whereas in **2** (due to termination of Zn centres of the T2 clusters with H₂O ligands) only connection through the metal linker was observed.

The accessible volume of **1**, not taking into account the $\text{Zn}(\text{H}_2\text{O})_4^{2+}$ cations, and its pore diameter (excluding van der

^a Department of Chemistry, 2145 Sheridan Road, Northwestern University, Evanston, IL 60208-3113, USA. E-mail: m-kanatzidis@northwestern.edu; Fax: +1 847-491-593; Tel: +1 847-467-1541

^b Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208-3113, USA

† Electronic supplementary information (ESI) available: Mid-infrared spectrum and TGA of (**1**) and its proton-exchanged analogue as well as the proton-exchange experimental part and details of the NLO, IR, PXRD, EDS, thermal analysis and ICP-AES measurements. See DOI: 10.1039/b712732d

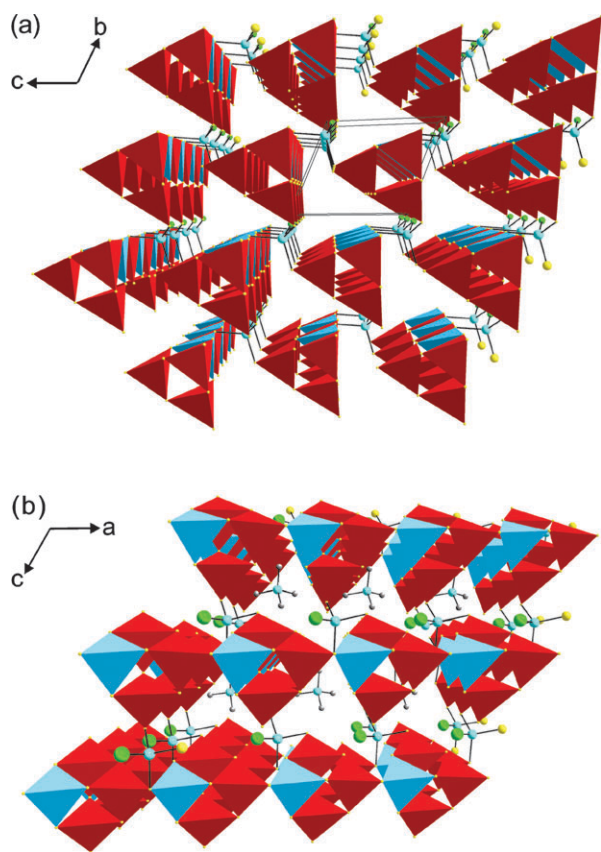


Fig. 1 (a) The framework of compound **1** viewed along the *a*-axis. The $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ extra-framework cations are omitted for clarity. The $[\text{ZnSn}_3\text{Se}_{10}]^{6-}$ T2 cluster units are represented using a polyhedral model (SnSe₄: red polyhedra; ZnSe₄: cyan polyhedra). The Zn (Zn₂) atoms linking the T2 units are shown as cyan balls. Se and methylamine nitrogen atoms are represented with yellow and green balls, respectively. Sn–Se and Zn–Se bond distances lie in the range 2.4736(13)–2.5539(14) Å and 2.4307(18)–2.5274(16) Å, respectively; (b) the framework of **1** viewed along the *b*-axis. The $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ cations located in the pores of the structure are represented with balls (Zn: cyan; O, grey) and sticks.

Waals radii) calculated by PLATON are 29% and 4.7 Å, respectively.¹⁶

The accessibility of the pores of **1** was probed using H⁺ ion exchange. The material displays amazing stability in extremely acidic environments (pH ~ 0). As confirmed by powder XRD data (Fig. 2), the structure of **1** remained intact even after treating it with 6 M HCl. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and energy dispersive spectroscopy (EDS) analysis on various proton-treated samples revealed a reduction of the Zn content of the material from 3 to ~2 per formula unit. This is consistent with the exchange of the extra-framework Zn²⁺ by H⁺. In addition, TGA measurements (see ESI†) revealed a substantial reduction of the water content of **1** after the proton-exchange process, which indicates the replacement of the $[\text{Zn}(\text{H}_2\text{O})_4]^{2+}$ complex by protons.

The proton-containing material (presumably $\text{H}_2[\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$) displays a significantly narrower energy band gap (1.76 eV) compared to the pristine material (2.08 eV), Fig. 3.

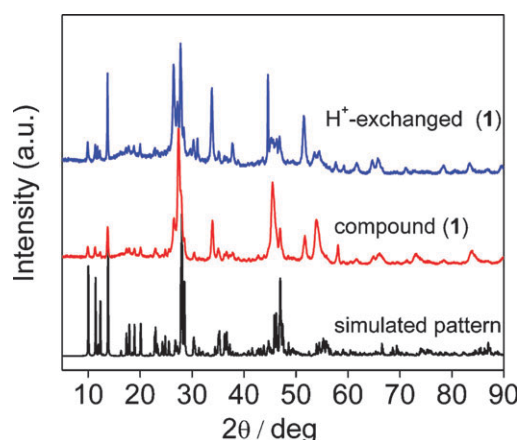


Fig. 2 X-Ray diffraction patterns of compound **1** and its proton-exchanged analogue as well as a simulated pattern based on the single crystal data XRD pattern of **1**.

As no significant contraction of the framework occurred after proton exchange (Fig. 2), the red shift in the band gap of the protonated material can be explained on the basis of bonding interactions of the protons with the Se atoms of the framework. These interactions are stronger than the purely electrostatic ones between $\text{Zn}(\text{H}_2\text{O})_4^{2+}$ and the framework.^{2f} Good acid stability seems to be a general property of many open framework selenides^{2d,2f,17} and may be useful for constructing a new family of proton conductors and Lewis acid catalysts.

The polar structure of **1**, along with its optically transparent nature and the high polarizability of its framework, make it attractive for NLO studies. SHG measurements were performed on polycrystalline samples of compound **1** with the modified Kurtz method¹⁸ (see ESI for details of the NLO measurements†). Using laser beams with 1200–2000 nm wavelengths, the material displayed a high SHG efficiency of $\sim 0.6 \times \text{AgGaSe}_2$ which is a commercial NLO material used for infrared applications.¹⁹ In addition, phase-matching experiments involving SHG intensity determination vs. particle size revealed that the material is type I phase-matchable (Fig. 4). Phase matching is a necessary property for NLO applications.

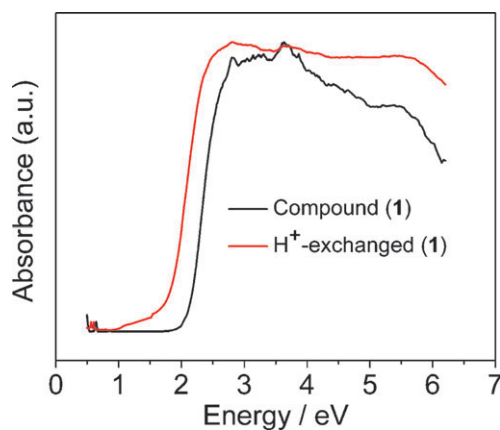


Fig. 3 Solid state NIR/UV-Vis absorption spectra for compound **1** and its proton-exchanged analogue.

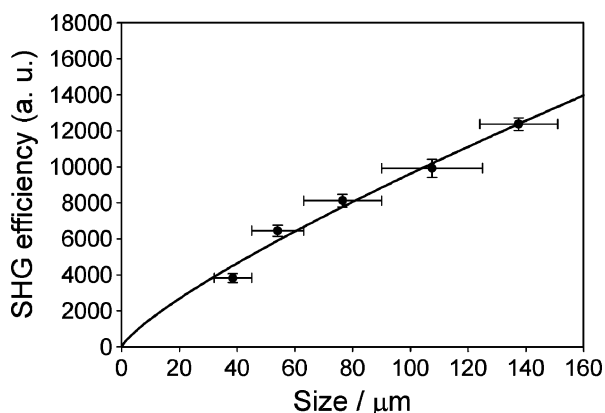


Fig. 4 SHG efficiency to particle size diagram of compound 1 showing type-I phase-matching. The line is only a guide for the eye.

In conclusion, the remarkable acid stability of the polar open framework chalcogenide $[\text{Zn}(\text{H}_2\text{O})_4][\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$ allows the isolation of the protonated analogue by an ion-exchange process. The framework features unprecedented tin–zinc T2 chalcogenide clusters exhibiting an unusual connectivity mode. The phase-matchable NLO properties associated with a large second harmonic generation response are comparable with those of commercial NLO chalcogenide materials.²⁰

Financial support from the National Science Foundation (DMR-0702911 and CHE-0211029 Chemistry Research Group) and the Northwestern MRSEC under NSF (DMR 9632472) are gratefully acknowledged. A portion of this work was completed at the Northwestern University Analytical Services Laboratory. A description of the facility and full funding disclosure can be found at <http://pyrite.chem-northwestern.edu/analyticalserviceslab/asl.htm>. This material is based upon work supported by IEC.

Notes and references

‡ Synthesis of $[\text{Zn}(\text{H}_2\text{O})_4][\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$ (1): elemental Sn (2 mmol, 0.239 g), Zn (2 mmol, 0.132 g), Se (6 mmol, 0.477 g) and methylamine (8 mL, 40% in water) were mixed in a 23 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in a temperature-controlled oven operated at 190 °C. The autoclave remained undisturbed at this temperature for 9 d. Then, the autoclave was allowed to cool at room temperature. An orange-red crystalline product was isolated by filtration (0.57 g, yield \approx 63 % based on Sn), washed several times with water, acetone and ether (in this order) and dried under vacuum. EDS analysis on various needle-shaped crystals gave the average formula “ $\text{Sn}_{2.8}\text{Zn}_{3.1}\text{Se}_{9.2}$ ”. C, H, N analysis, found (%): C, 0.66; H, 0.56; N, 1.20. Calculated (%) for $\text{CH}_9\text{O}_4\text{NZn}_3\text{Sn}_3\text{Se}_9$: C, 0.88; H, 0.88; N, 1.03.

§ Single crystal X-ray diffraction intensity data were collected at 298 K on a Bruker SMART platform CCD diffractometer with Mo-K α ($\lambda = 0.71073$ Å) radiation. An empirical absorption correction was applied to the data using SADABS. The structure was solved with direct methods using SHELX-97. Crystals of $[\text{Zn}(\text{H}_2\text{O})_4][\text{Zn}_2\text{Sn}_3\text{Se}_9(\text{MeNH}_2)]$ belong to the space group $P1$ (no. 1) with $a = 7.8632(12)$ Å, $b = 8.6162(13)$ Å, $c = 10.2185(15)$ Å, $V = 582.04(15)$ Å³, $\alpha = 105.74(0)^\circ$, $\beta = 110.63(0)^\circ$, $\gamma = 103.17(0)^\circ$. Other crystal data: $Z = 1$, $\text{FW} = 1365.95$, $D_c = 3.897$ g cm⁻³, $\mu = 20.28$ mm⁻¹; total reflections 5970, independent reflections 4650, parameters 183, Flack parameter = 0.044(11), ($R_{\text{int}} = 0.0368$); $R1 = 0.0372$, $wR2 = 0.0812$, $\text{GOF} = 0.939$. CCDC 657916. For crystallographic data in CIF format see DOI: 10.1039/b712732d

- R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett and E. M. Flanigen, in *Zeolites: Facts, Figures, Future, Proceedings of the 8th International Zeolite Conference*, ed. P. A. Jacobs and R. A. van Santen, Elsevier, Amsterdam, 1989, pp. 375–387.
- (a) S. Dhingra and M. G. Kanatzidis, *Science*, 1992, **258**, 1769; (b) N. Ding, D. Y. Chung and M. G. Kanatzidis, *Chem. Commun.*, 2004, 1170; (c) M. J. Manos, R. G. Iyer, E. Quarez, J. H. Liao and M. G. Kanatzidis, *Angew. Chem., Int. Ed.*, 2005, **44**, 3552; (d) N. Ding and M. G. Kanatzidis, *Angew. Chem., Int. Ed.*, 2006, **45**, 1397; (e) M. J. Manos, K. Chrissafis and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2006, **128**, 8875; (f) M. J. Manos, C. D. Malliakas and M. G. Kanatzidis, *Chem.–Eur. J.*, 2007, **13**, 51.
- (a) O. M. Yaghi, Z. Sun, D. A. Richardson and T. L. Groy, *J. Am. Chem. Soc.*, 1994, **116**, 807; (b) H. L. Li, M. Eddaoudi, A. Laine, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 6096; (c) H. L. Li, A. Laine, M. O’Keeffe and O. M. Yaghi, *Science*, 1999, **283**, 1145.
- (a) N. F. Zheng, X. G. Bu, B. Wang and P. Y. Feng, *Science*, 2002, **298**, 2366; (b) N. F. Zheng, X. H. Bu and P. Y. Feng, *Nature*, 2003, **426**, 428; (c) N. F. Zheng, X. H. Bu and P. Y. Feng, *J. Am. Chem. Soc.*, 2003, **125**, 1138; (d) N. F. Zheng, X. H. Bu and P. Y. Feng, *Chem. Commun.*, 2005, 2805; (e) N. Zheng, X. H. Bu, H. Vu and P. Y. Feng, *Angew. Chem., Int. Ed.*, 2005, **44**, 5299.
- (a) C. L. Cahill, Y. H. Ko and J. B. Parise, *Chem. Mater.*, 1998, **10**, 19; (b) C. L. Cahill, B. Gugliotta and J. B. Parise, *Chem. Commun.*, 1998, 1715; (c) C. L. Cahill and J. B. Parise, *J. Chem. Soc., Dalton Trans.*, 2000, 1475.
- W. P. Su, X. Y. Huang, J. Li and H. X. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 12944.
- (a) C. Zimmermann, M. Melullis and S. Dehnen, *Angew. Chem., Int. Ed.*, 2002, **41**, 4269; (b) M. K. Brandmayer, R. Clerac, F. Weigend and S. Dehnen, *Chem.–Eur. J.*, 2004, **10**, 5147; (c) M. Melullis, R. Clerac and S. Dehnen, *Chem. Commun.*, 2005, 6008.
- (a) T. Jiang, G. A. Ozin and R. L. Bedard, *Adv. Mater.*, 1994, **6**, 860; (b) H. Ahari, A. Lough, S. Petrov, G. A. Ozin and R. L. Bedard, *J. Mater. Chem.*, 1999, **9**, 1263.
- S. Bag, P. N. Trikalitis, P. J. Chupas, G. S. Armatas and M. G. Kanatzidis, *Science*, 2007, **317**, 490.
- M. E. Davis, *Nature*, 2002, **417**, 813.
- M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O’Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
- J. H. Liao, G. M. Marking, K. F. Hsu, Y. Matsushita, M. D. Ewbank, R. Borwick, P. Cunningham, M. J. Rosker and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2003, **125**, 9484.
- P. Y. Feng, X. H. Bu and N. F. Zheng, *Acc. Chem. Res.*, 2005, **38**, 293.
- It was not possible to locate by single crystal X-ray analysis the methyl group of the methylamine (MA) ligand. This is attributed to positional disorder associated with rotation around the Zn–N bond. The presence of MA was confirmed by IR spectroscopy (see ESI[†]), pyrolysis–mass spectrometry and C, H, N analysis.† A mixed N/O occupancy model for the X-ray refinement of compound 1 was not successful. The assignment of the positions for the methylamine nitrogen and water oxygen atoms was done based on (a) the Zn–N bond distance [2.091(10) Å] being, as expected, longer than the Zn–O distances [2.019(12)–2.059(10) Å] and (b) the TGA measurements revealing removal of four water molecules in a single step, which indicates a similar chemical environment for these molecules.
- (a) X.-B. Cui, J.-Q. Xu, L. Ding, H. Ding, L. Ye and G.-Y. Yang, *J. Mol. Struct.*, 2003, **660**, 131; (b) W. Chen, N. Li and S. Xiang, *J. Solid State Chem.*, 2004, **177**, 3229.
- (a) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2005; (b) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- P. N. Trikalitis, N. Ding, C. Malliakas, S. J. L. Billinge and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2004, **126**, 15326.
- S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
- D. N. Nikogosyan, *Nonlinear Optical Crystals: A Complete Survey*, Springer-Science, New York, USA, 2005.
- (a) R. L. Bayer, *Annu. Rev. Mater. Sci.*, 1974, **4**, 147; (b) P. G. Schunemann, *Proc. SPIE–Int. Soc. Opt. Eng.*, 2007, **6455**, 64550R1.