

single bonds that are formed with a Pd complex as a template, which can now be incorporated to the gallery of other σ bonds that are known to coordinate to transition metals: H–H, C–H, Si–H, Ge–H, Sn–H, and B–H. The present study also suggests that the structure of a related dinuclear Ni complex^[19] should be revisited and reinterpreted, and might be considered as the first structurally characterized example of such kind of novel coordination of Si–Si bonds.

Received: April 1, 2002 [Z18962]

- [1] W. Chen, S. Shimada, M. Tanaka, *Science* **2002**, 295, 308.
- [2] R. H. Crabtree, *Science* **2002**, 295, 288.
- [3] N. Kleiner, M. Dräger, *J. Organomet. Chem.* **1984**, 270, 151.
- [4] N. Wiberg, H. Schuster, A. Simon, K. Peters, *Angew. Chem.* **1986**, 98, 100; *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 79.
- [5] N. Wiberg, W. Nidenmayer, *Z. Naturforsch. B* **2000**, 55, 389.
- [6] H. Zabrodsky, S. Peleg, D. Avnir, *J. Am. Chem. Soc.* **1992**, 114, 7843.
- [7] H. Zabrodsky, S. Peleg, D. Avnir, *J. Am. Chem. Soc.* **1993**, 115, 8278 (Erratum: H. Zabrodsky, S. Peleg, D. Avnir, *J. Am. Chem. Soc.* **1994**, 116, 656).
- [8] S. Alvarez, D. Avnir, M. Llunell, M. Pinsky, *New J. Chem.* **2002**, in press.
- [9] E. A. Boudreaux, L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, Wiley, New York, **1976**.
- [10] The structures were optimized at the B3LYP level of theory implemented in Gaussian98 (Revision A.11).^[10a] Effective core potentials and their associated double- ζ basis set LANL2DZ were used for Pd, P, and Si atoms, supplemented with polarization functions for Si and P, whereas a 6-31G basis set was used for H and C. The structures shown in Figure 1b–c have been characterized as energy minima through vibrational frequencies calculations. Interaction energies were corrected for the basis set superposition error by means of the counterpoise method; a) Gaussian98 (Revision A.11), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [11] F. Maseras, A. Lledós, E. Clot, O. Eisenstein, *Chem. Rev.* **2000**, 100, 601.
- [12] G. J. Kubas, *Metal Dihydrogen and σ -Bond Complexes*, Kluwer Academic/Plenum Publishers, New York, **2001**.
- [13] G. J. Kubas, *J. Organomet. Chem.* **2001**, 635, 37.
- [14] G. I. Nikonov, *J. Organomet. Chem.* **2001**, 635, 24.
- [15] G. I. Nikonov, *Angew. Chem.* **2001**, 113, 3457; *Angew. Chem. Int. Ed.* **2001**, 40, 3353.
- [16] D. R. Evans, T. Drovetskaya, R. Bau, C. A. Reed, P. D. W. Boyd, *J. Am. Chem. Soc.* **1997**, 119, 3633.
- [17] F. Delpech, S. Sabo-Etienne, J.-C. Daran, B. Chaudret, K. Hussein, C. J. Marsden, J.-C. Barthelat, *J. Am. Chem. Soc.* **1999**, 121, 6668.
- [18] H. Hashimoto, Y. Sekiguchi, T. Iwamoto, C. Kabuto, M. Kira, *Organometallics* **2002**, 21, 454.
- [19] S. Shimada, M. L. N. Rao, T. Hayashi, M. Tanaka, *Angew. Chem.* **2001**, 113, 219; *Angew. Chem. Int. Ed.* **2001**, 40, 213.
- [20] T. Kusukawa, Y. Kabe, B. Nestler, W. Ando, *Organometallics* **1995**, 14, 2556.
- [21] G. I. Nikonov, S. F. Vyobishchikov, L. G. Kuzmina, J. A. K. Howard, *Chem. Commun.* **2002**, 568.
- [22] C. A. Bayse, M. B. Hall, *J. Am. Chem. Soc.* **1999**, 121, 1348.
- [23] L. Andrews, X. Wang, M. E. Alikhani, L. Manceron, *J. Phys. Chem. A* **2001**, 105, 3052.
- [24] Similar conclusions have been reached independently by Cramer and co-workers E. C. Sherer, C. R. Kinsinger, B. L. Kormos, J. D. Thompson, C. J. Cramer, *Angew. Chem.* **2002**, 114, 2033; *Angew. Chem. Int. Ed.* **2002**, 41, 1953.

A 3D Open-Framework Indium Telluride and Its Selenide and Sulfide Analogues**

Cheng Wang, Xianhui Bu, Nanfeng Zheng, and Pingyun Feng*

There has been increasing interest in designing host–guest materials with crystalline conducting frameworks.^[1] The combination of porosity and conductivity in the same material is expected to lead to unique properties suitable for electronic applications as well as molecular-sieve type applications. One application that might be envisioned to benefit from the development of host–guest chalcogenide open frameworks is in the area of thermoelectric materials, where there has been interest in developing host–guest order–disorder materials.^[2] The disordered portion of the structure is expected to scatter phonons and minimize lattice thermal conductivity while the ordered crystalline framework serves to maintain high electric conductivity.^[3] The recent interest in host–guest germanium–silicon clathrates reflects the application of this design strategy.^[4, 5]

So far, extensive studies have been made with purely inorganic chalcogenides because of their useful optoelectronic and thermoelectric properties.^[6] For example, CuInSe₂ is among the most efficient photovoltaic materials and Bi₂Te₃ is one of the best thermoelectric materials. In comparison, very little research has been done on the optical, electronic, and thermoelectric properties of open-framework chalcogenides. This is in part a result of the rarity of host–guest heavy-chalcogenide open frameworks. To our knowledge, no amine-templated 3D open-framework tellurides have been made prior to this work, even though some open-framework sulfides and selenides are already known.^[7–11]

In the synthesis of metal-chalcogenide open-framework materials, small clusters are often found to serve as structural building units (SBUs) in extended frameworks. These clusters include supertetrahedral T₂ (M₄X₁₀), T₃ (M₁₀X₂₀), and T₄ (M₂₀X₃₅), where M is a metal ion and X is a chalcogen anion.^[12, 13] While the cluster-based structural-design approach is known to generate large pores,^[12, 13] the intercluster connection is typically provided by a single atom. This situation may not represent the best configuration for electronic properties, therefore, it is highly desirable to have open-framework chalcogenides with topological features that extend beyond the cluster-based configurations.

Here we report an amine-directed, chain-based 3D telluride open framework together with its selenide and sulfide analogues. It is also demonstrated here that mixed-chalcoge-

[*] Prof. P. Feng, Dr. C. Wang, N. Zheng
Department of Chemistry
University of California
Riverside, CA 92521 (USA)
Fax: (+1) 909-787-4713
E-mail: pingyun.feng@ucr.edu
Dr. X. Bu
Department of Chemistry
University of California
Santa Barbara, CA 93106 (USA)

[**] We thank UC Riverside, UC Energy Institute, and the donors of The Petroleum Research Fund (administered by the ACS) for funding.

nide open frameworks with various compositions can be made. These open-framework chalcogenides have the same framework connectivity and are collectively called UCR-2 (see Table 1). The smallest integral unit ($\text{In}_{33}\text{X}_{56}$, $\text{X} = \text{S}, \text{Se}, \text{Te}, \text{S/Se}, \text{and S/Te}$) in these compounds has 89 atoms and is very large compared to similar units in reported open framework sulfides. These structures are in general more complex than cluster-based frameworks and they offer additional opportunities to study the structure–property correlation in open-framework chalcogenides.

Table 1. A summary of crystallographic data for selected open-framework chalcogenides synthesized in this study.^[a]

Name ^[b]	Framework formula	<i>a</i> [Å]	<i>c</i> [Å]	<i>R</i> (<i>F</i>)	2 θ_{max}
UCR-2InS-TMDP	($\text{In}_{33}\text{S}_{56}$) ¹³⁻	21.650(1)	33.610(2)	5.54	50
UCR-2InSe-DIPA	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.455(3)	34.335(6)	5.69	45
UCR-2InSe-TETA	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.344(3)	34.100(5)	4.18	45
UCR-2InSe-TAA	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.54(1)	34.09(1)		
UCR-2InSe-AEAE	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.333(5)	34.397(9)		
UCR-2InSe-DPA	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.370(6)	34.355(9)		
UCR-2InSe-TMHD	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.476(7)	34.29(1)		
UCR-2InSe-BAPP	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.69(1)	34.71(2)		
UCR-2InSe-TOTD	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.566(8)	34.701(9)		
UCR-2InSe-HMI	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.493(3)	34.281(5)		
UCR-2InSe-DAO	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.254(3)	34.144(7)		
UCR-2InSe-DMMP	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.256(7)	34.23(2)		
UCR-2InSe-APM	($\text{In}_{33}\text{Se}_{56}$) ¹³⁻	22.322(6)	34.46(2)		
UCR-2InTe-TETA	($\text{In}_{33}\text{Te}_{56}$) ¹³⁻	23.710(5)	36.076(9)		
UCR-2InTe-APDA	($\text{In}_{33}\text{Te}_{56}$) ¹³⁻	23.619(3)	36.370(7)	4.78	45
UCR-2InTe-TAA	($\text{In}_{33}\text{Te}_{56}$) ¹³⁻	23.912(4)	35.910(7)	6.40	45
UCR-2InS ₂ Te-APDA	($\text{In}_{33}\text{S}_{16}\text{Te}_{40}$) ¹³⁻	22.653(11)	34.115(23)	7.74	42
UCR-2InS ₂ Se-TMDP	($\text{In}_{33}\text{S}_{16}\text{Se}_{40}$) ¹³⁻	22.037(4)	34.101(9)	6.03	45
UCR-2InS ₂ Se-DIPA	($\text{In}_{33}\text{S}_{16}\text{Se}_{40}$) ¹³⁻	22.354(4)	34.337(9)	5.51	45

[a] Crystal structures were solved from single-crystal data collected at 298 K on a SMART CCD diffractometer with $\text{MoK}\alpha$. The space group is *R*32 for all structures and $Z=3$. $R(F)=\sum||F_o|-|F_c||/\sum|F_o|$ with $F_o>4.0\sigma(F)$.

[b] TMDP = 4,4'-trimethylenedipiperidine, $\text{C}_{13}\text{H}_{26}\text{N}_2$; DIPA = diisopropylamine, $\text{C}_6\text{H}_{15}\text{N}$; APDA = *N*-(2-aminoethyl)-1,3-propanediamine, $\text{C}_5\text{H}_{15}\text{N}_3$; TETA = triethylenetetramine, $\text{C}_6\text{H}_{18}\text{N}_4$; TAA = tris(2-aminoethyl)amine, $\text{C}_6\text{H}_{18}\text{N}_4$; AEAE = 2-(2-aminoethylaminoethanol), $\text{C}_4\text{H}_{12}\text{N}_2\text{O}$; DPA = dipropylamine, $\text{C}_6\text{H}_{15}\text{N}$; BAPP = 1,4-bis(3-aminopropyl)piperazine, $\text{C}_{10}\text{H}_{24}\text{N}_4$; TMHD = C,C,C-trimethyl-1,6-hexanediamine, $\text{C}_9\text{H}_{22}\text{N}_2$; TOTD = 4,7,10-trioxa-1,13-tridecanediamine, $\text{O}[\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2)_3\text{NH}_2]_2$; HMI = hexamethylenimine, $\text{C}_6\text{H}_{13}\text{N}$; DAO = 1,8-diaminooctane, $\text{C}_8\text{H}_{20}\text{N}_2$; DMMP = 2,6-dimethylmorpholine, $\text{C}_6\text{H}_{13}\text{NO}$; APM = *N*-(3-aminopropyl)morpholine, $\text{C}_7\text{H}_{16}\text{N}_2\text{O}$.

Unlike the known sulfide open frameworks that contain building units related to adamantane clusters, the 3D framework in the UCR-2 family of materials is constructed from the cross-linking of helical chains. Therefore, the synthesis of UCR-2 demonstrates the feasibility of creating open-framework chalcogenides without the use of supertetrahedral clusters.

To prepare crystals of UCR-2InTe-APDA, *N*-(2-aminoethyl)-1,3-propanediamine (APDA) was added to a 23 ml-Teflon-lined stainless steel autoclave containing 3.264 g of water until the pH of the solution was 13.50. Indium metal (84 mg) and tellurium (187 mg) were then added. The vessel was sealed and heated at 200 °C for 10 days. The autoclave was subsequently allowed to cool to room temperature.

With proper choice of the solution pH value and structure-directing agents, both sulfide and selenide analogues (see Table 1) can be synthesized under similar conditions. In

addition, mixed chalcogenides with more than one chalcogen type in the inorganic framework (e.g., S/Se, S/Te) have also been synthesized. Crystals are pale yellow, orange-red, and dark red for sulfides, selenides, and tellurides, respectively, demonstrating the variation in their electronic bandgap.

While all the framework atoms can be determined unambiguously in all the structures (Figure 1), guest amine molecules are disordered inside large cavities and can not be located. The presence of organic molecules is verified by

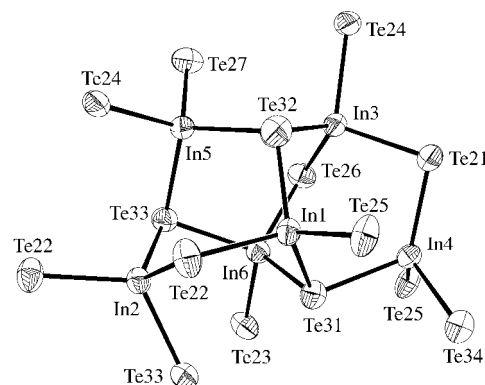


Figure 1. The ORTEP view of coordination environments for In and Te atoms in UCR-2InTe-APDA. (thermal ellipsoids set at the 50 % level).^[19]

elemental analysis.^[14] The disorder of the amine molecules may be related to the relatively weak host–guest interaction in open-framework chalcogenides. In particular, the hydrogen bonding (i.e. $\text{N-H}\cdots\text{X}$, $\text{X} = \text{S}, \text{Se}, \text{or Te}$) is considerably weaker than the $\text{N-H}\cdots\text{O}$ type of hydrogen bonding that is often responsible for the ordering of guest amine molecules in oxides.^[15, 16] When these extra-framework species are not considered, by using the program PLATON^[17] the porosity of UCR-2InS-TMDP is calculated to be 50 %.

When divalent metal cations are included in the synthesis mixture for UCR-2InS-TMDP, the formation of UCR-2InS-TMDP is suppressed and another type of framework containing supertetrahedral T4 clusters ($\text{M}_4\text{In}_{16}\text{S}_{33}$)¹⁰⁻ ($\text{M} = \text{Mn}, \text{Co}, \text{Fe}, \text{Zn}, \text{Cd}$, denoted collectively as UCR-1MInS) is formed.^[13] The addition of these divalent metal cations, however, does not have an effect on the formation of UCR-2 selenide and telluride analogues. It can be inferred that selenides and tellurides have a stronger tendency to form non-cluster-based open frameworks than sulfides.

Instead of forming a cluster that would resemble a fragment of the cubic ZnS type structure, InX_4 tetrahedra in UCR-2 share corners to form infinite chains (Figure 2 and Figure 3). Chains are cross-linked to give a 3D framework with large cages. Cages are interconnected to form a 3D channel system.

Noteworthy is that the T-X-T angles vary from 96.8–112.9° for the sulfide, 93.3–110.3° for the selenide, and 92.6–108.2° for the telluride. This is a range of up to 17°. While this range is small compared to the range of T-O-T angles (T = tetrahedral atom) in zeolites it is considerably greater than the 5° range (i.e., 103–108°) of T-S-T angles in some Ge–S compounds.^[7] This observation suggests that there could be a richer structural diversity in indium chalcogenides than in

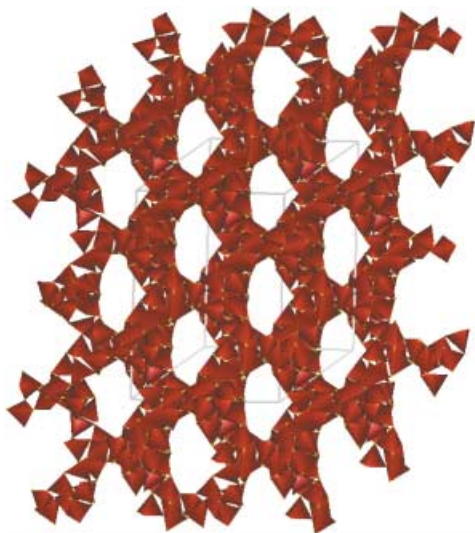


Figure 2. A polyhedral view of the 3D framework of UCR-2InTe-APDA showing the formation of cages by the fusion of chains propagating along the *c* axis.^[19]

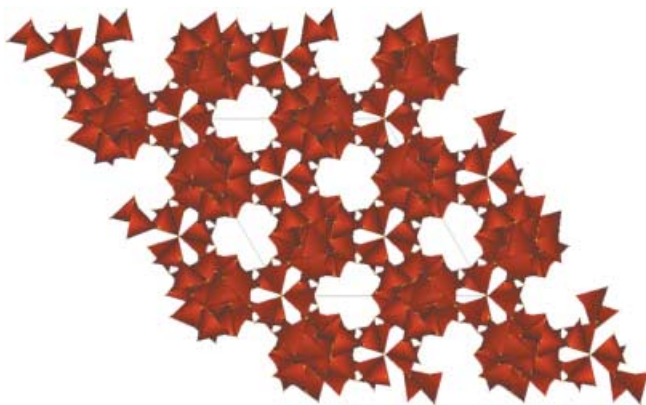


Figure 3. A polyhedral view of the 3D framework of UCR-2InTe-APDA projected down the *c* axis.^[19]

other chalcogenides. It is also apparent that the T-X-T angle becomes smaller for heavier chalcogens. However, compared to the significant change in the T-X-T angle from oxides (about 140°) to sulfides (about 106°), the change in the T-X-T angle from sulfides (about 106°) to tellurides (about 100°) is relatively minor. This situation suggests that the structural properties of open-framework sulfides, selenides, and tellurides should be quite similar and are significantly different from those of oxides.

In mixed compounds with more than one type of chalcogen ions, the distribution of different chalcogen ions among crystallographic sites is not random as shown by the refined occupancy factors. For example, in UCR-2InTe-APDA, the tricoordinate chalcogen sites are occupied by light sulfur atoms. In the bicoordinate chalcogen sites, the refined occupancies show that about 56% of atoms are tellurium ions (the S:Te molar ratio = 1:1 in the synthesis mixture). The overall S:Te atomic ratio of 1.76:1 derived from the occupancy refinement agrees well with the measurement (1.70:1) obtained from the energy-dispersive spectrum collected by scanning electron microscopy.

Fluorescent spectra were measured on a SPEX Fluorolog-3 system equipped with a 450 W xenon lamp. For UCR-2InS-TMDP, a broad emission centered at 520 nm was observed when excited at 470 nm. For UCR-2InSe-BAPP, the emission was centered at 563 nm when excited at 482 nm. Compared to open-framework oxides such as phosphates and germanates with typical absorption and emission maxima at 360 nm and 410 nm, respectively,^[18] it is apparent that there is a systematic variation in the spectral characteristics of these open-framework materials. It can be anticipated that by varying the topologies and compositions of open-framework chalcogenides, photoluminescent materials with a wide range of emission characteristics may be developed.

In conclusion, we have shown that a family of chalcogenides, tellurides in particular, have been synthesized and structurally characterized. The framework composition is highly flexible and controllable. The unique host–guest, order–disorder features may make them useful for studies in semiconductor applications, for example, in the development of a new class of semiconducting materials based on heavy-chalcogenide host–guest open-framework materials.

Received: February 13, 2002 [Z 18703]

- [1] A. K. Cheetham, G. Ferey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268.
- [2] T. M. Tritt, *Science* **1999**, *283*, 804.
- [3] J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, G. A. Slack, *Phys. Rev. Lett.* **1999**, *82*, 779.
- [4] G. S. Nolas, J. J. Cohn, G. A. Slack, S. B. Schuiman, *Appl. Phys. Lett.* **1998**, *73*, 178.
- [5] S. Lattner, X. Bu, N. Blake, H. Metiu, G. D. Stucky, *J. Solid State Chem.* **2000**, *151*, 61.
- [6] D. Chung, T. Hogan, P. Brazis, M. Rocci-Lane, C. Kannewurf, M. Bastea, C. Uher, M. G. Kanatzidis, *Science* **2000**, *287*, 1024.
- [7] R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett, E. M. Flanigen, in *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference* (Eds.: P. A. Jacobs, R. A. van Santen), Elsevier, Amsterdam, **1989**, p. 375.
- [8] H. Li, J. Kim, T. L. Groy, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4867.
- [9] C. L. Cahill, Y. Ko, J. B. Parise, *Chem. Mater.* **1998**, *10*, 19.
- [10] H. Ahari, A. Garcia, S. Kirby, G. A. Ozin, D. Young, A. J. Lough, *J. Chem. Soc. Dalton Trans.* **1998**, 2023.
- [11] H. Ahari, A. Lough, S. Petrov, G. A. Ozin, R. L. Bedard, *J. Mater. Chem.* **1999**, *9*, 1263.
- [12] H. Li, A. Laine, M. O'Keeffe, O. M. Yaghi, *Science* **1999**, *283*, 1145.
- [13] C. Wang, Y. Li, X. Bu, N. Zheng, O. Zivkovic, C. Yang, P. Feng, *J. Am. Chem. Soc.* **2001**, *123*, 11 506.
- [14] Elemental analysis (%) calcd for UCR-2InS-TMDP based on the formula $[\text{In}_{33}\text{S}_{56}](\text{C}_{13}\text{H}_{26}\text{N}_2\text{H}_2)_{6.5}$: C 14.57, H 2.63, N 2.61; found: C 14.16, H 2.06, N 2.57; (%) calcd for UCR-2InSe-BAPP based on the formula $[\text{In}_{33}\text{Se}_{56}](\text{C}_{10}\text{H}_{24}\text{N}_4\text{H}_2)_{6.5}$: C 8.19, H 1.79, N 3.82; found: C 9.02, H 1.81, N 3.43; (%) calcd for UCR-2InTe-APDA based on the formula $[\text{In}_{33}\text{Te}_{56}](\text{C}_5\text{H}_{15}\text{N}_3\text{H}_3)(\text{C}_5\text{H}_{15}\text{N}_3\text{H}_2)_5$: C 3.09, H 0.95, N 2.16; found: C 2.94, H 0.84, N 1.43.
- [15] P. Feng, X. Bu, G. D. Stucky, *Nature* **1997**, *388*, 735.
- [16] W. T. A. Harrison, M. L. F. Phillips, T. M. Nenoff, E. J. MacLean, S. J. Teat, R. S. Maxwell, *J. Chem. Soc. Dalton Trans.* **2001**, *5*, 546.
- [17] A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.
- [18] P. Feng, *Chem. Commun.* **2001**, 1668.
- [19] CCDC-179232 – CCDC-179234 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).