single bonds that are formed with a Pd complex as a template, which can now be incorporated to the gallery of other d complexes 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 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 [Z.1862]


[11] The structures were optimized at the B3LYP level of theory implemented in Gaussian98 (Revision A.11).\[11\] Effective core potentials and their associated double-\(\tilde{\text{c}}\) 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 frequency 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. Clioford, 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. Komarov, 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. Reploge, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.


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 (In$_3$X$_{56}$, X = S, Se, Te, S/Se, 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.

Unlike the known sulfide open frameworks that contain sulfur and selenides and tellurides have a stronger tendency to form non-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. In particular, the hydrogen bonding (i.e. N-H···X, X = S, Se, or Te) is considerably weaker than the N-H···O type of hydrogen bonding that is often responsible for the ordering of guest amine molecules in oxides. When these extra-framework species are not considered, by using the program PLATON when the crystal structure contains more than one chalcogen (S, Se, or Te) is considerably greater than the 5° range (i.e., 103°–108°) of T-S-T angles in some Ge–S compounds. This observation suggests that there could be a richer structural diversity in indium chalcogenides than in elemental analysis. The disorder of the amine molecules may be related to the relatively weak guest–host interaction in open-framework chalcogenides. In particular, the hydrogen bonding (i.e. N-H···X, X = S, Se, or Te) is considerably weaker than the N-H···O type of hydrogen bonding that is often responsible for the ordering of guest amine molecules in oxides. When these extra-framework species are not considered, using the program PLATON when the crystal structure contains more than one chalcogen (S, Se, or Te) is considerably greater than the 5° range (i.e., 103°–108°) of T-S-T angles in some Ge–S compounds. This observation suggests that there could be a richer structural diversity in indium chalcogenides than 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

### Table 1. A summary of crystallographic data for selected open-framework chalcogenides synthesized in this study.

<table>
<thead>
<tr>
<th>Name[a]</th>
<th>Framework formula</th>
<th>α [°]</th>
<th>c [Å]</th>
<th>R(F)</th>
<th>2θ$_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCR-2In-S-TMDP</td>
<td>(In$<em>3$S)$</em>{56}$</td>
<td>21.650(1)</td>
<td>33.610(2)</td>
<td>5.54</td>
<td>50</td>
</tr>
<tr>
<td>UCR-2In-Se-DIPA</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.455(3)</td>
<td>34.335(6)</td>
<td>5.69</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-TETA</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.344(3)</td>
<td>34.100(5)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-TAA</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.54(1)</td>
<td>34.09(1)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-AEAE</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.333(5)</td>
<td>34.397(9)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-DPA</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.370(6)</td>
<td>34.355(9)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-TMHD</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.476(7)</td>
<td>34.29(1)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-BAPP</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.69(1)</td>
<td>34.71(2)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-TODT</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.566(8)</td>
<td>34.70(1)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-HMI</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.493(3)</td>
<td>34.28(1)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-DAO</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.254(3)</td>
<td>34.14(7)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-DMMMP</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.256(7)</td>
<td>34.23(2)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-APM</td>
<td>(In$<em>3$Se)$</em>{56}$</td>
<td>22.322(6)</td>
<td>34.46(2)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-TETA</td>
<td>(In$<em>3$Te)$</em>{56}$</td>
<td>23.710(5)</td>
<td>36.07(9)</td>
<td>4.18</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-APDA</td>
<td>(In$<em>3$Te)$</em>{56}$</td>
<td>23.619(3)</td>
<td>36.37(7)</td>
<td>4.78</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-TAA</td>
<td>(In$<em>3$Te)$</em>{56}$</td>
<td>23.912(4)</td>
<td>35.91(7)</td>
<td>4.60</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-APDA</td>
<td>(In$<em>3$S)$</em>{56}$</td>
<td>22.653(11)</td>
<td>34.11(23)</td>
<td>7.74</td>
<td>42</td>
</tr>
<tr>
<td>UCR-2In-Se-TMDP</td>
<td>(In$<em>3$S)$</em>{56}$</td>
<td>22.037(4)</td>
<td>34.10(9)</td>
<td>6.03</td>
<td>45</td>
</tr>
<tr>
<td>UCR-2In-Se-DIPA</td>
<td>(In$<em>3$S)$</em>{56}$</td>
<td>22.354(4)</td>
<td>34.33(7)</td>
<td>5.51</td>
<td>45</td>
</tr>
</tbody>
</table>

[a] Crystal structures were solved from single-crystal data collected at 298 K on a SMART CCD diffractometer with Mo Kα. The space group is R32 for all structures and Z = 3. R(F) = Σ |F$_{o}$| - |F$_{c}$| / Σ |F$_{o}$| with F$_{c}$ > 4.00(F$_{o}$).

[b] TMDP = 4,4′-trimethylene bispyridine, C$_{13}$H$_{15}$N$_{2}$, DIPA = diisopropylamine, C$_{5}$H$_{15}$N$_{2}$, APD = N-(2-aminoethyl)-1,3-propanediamine, C$_{10}$H$_{22}$N$_{2}$, TETA = triethylenetetramine, C$_{12}$H$_{24}$N$_{4}$, TAA = tris(2-aminoethyl)amine, C$_{12}$H$_{24}$N$_{3}$, AEA = 2-(2-aminoethylaminoethanol), C$_{12}$H$_{26}$NO, DPA = dipropylamine, C$_{9}$H$_{19}$N$_{2}$, BAPP = 1,4-bis(2-amino) pyrrolizine, C$_{12}$H$_{17}$N$_{2}$, TDMMP = C$_{10}$C$_{13}$N$_{6}$, H$_{2}$NH, TOTD = 4,10-trioxa-1,13-tridecanediamine, O(CH$_{2}$O)$_{10}$CH$_{3}$H$_{3}$N$_{2}$, HMI = hexamethylenelimine, C$_{12}$H$_{24}$N$_{2}$, DAO = 1,8-diamo-noctoate, C$_{12}$H$_{24}$N$_{2}$, DMMMP = 2,6-dimethylmorpholine, C$_{10}$H$_{22}$N$_{1}$, APM = N-(3-aminopropyl)morpholine, C$_{15}$H$_{30}$N$_{3}$, O.

Figure 1. The ORTEP view of coordination environments for In and Te atoms in UCR-2InTe-APDA. (thermal ellipsoids set at the 50% level).
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,[13] 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 [Z18703]

[14] Elemental analysis (%) caled for UCR-2InS-TMDP based on the formula [In33S60](C11H15N3H3)5H2: C 15.74, H 2.63, N 3.26; found: C 15.74, H 2.63, N 3.26. (% caled for UCR-2InSe-BAPP based on the formula [In33Se60](C11H15N3H3)5H2: C 15.74, H 2.63, N 3.26; found: C 15.74, H 2.63, N 3.26.
[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).