metal-organic compounds

{[SmCl(en)$_4$][In$_2$Te$_4$]}$_n$: an indium telluride with a one-dimensional sinusoidal chain

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The title compound, *catena*-poly[[chloridotetrakis(ethylene-diamine-$\kappa^2 N,N'$)samarium(III)] [indium(III)-di-μ-tellurido-indium(III)-di-μ-tellurido]], {[SmCl(C$_2$H$_8$N$_2$)$_4$][In$_2$Te$_4$]}$_n$, consists of a one-dimensional sinusoidal {[InTe$_2$]$^-$}$_n$ anionic chain and [SmCl(en)$_4$]$^{2+}$ cations (en is ethylenediamine). The only other previously reported lanthanide analogue, *viz.* [LaCl-(en)$_4$][In$_2$Te$_4$], contains more usual linear one-dimensional {[InTe$_2$]$^-$}$_n$ anion chains [Chen, Li, Chen & Proserpio (1998). *Inorg. Chim. Acta*, **273**, 255–258]. The one-dimensional polymeric {[InTe$_2$]$^-$}$_n$ chain is built of InTe$_4$ tetrahedra sharing opposite edges. The Sm^{III} ion in the [SmCl(en)$_4$]$^{2+}$ cation is nine-coordinated by eight N atoms from four bidentate en molecules and by one chloride ion to form a monocapped square-antiprismatic geometry. The presence or absence of N—H···Cl hydrogen bonding is shown to affect the conformation of the anion.

Comment

The number of hybrid organic–inorganic indium chalcogen-ides has increased rapidly in recent years, owing to their potential applications in catalysis and in semiconductor and photoelectric chemistry (Zheng *et al.*, 2005; Li *et al.*, 1999; Manos *et al.*, 2007; Ding *et al.*, 2006; Rangan *et al.*, 2000). These compounds have usually been prepared at moderate temperatures (room temperature or under mild hydro- or solvothermal conditions) in the presence of an organic base as a structure-directing or templating agent. In the family of indium tellurides, many related compounds with a variety of structures have been reported, as exemplified by zero-dimensional molecular K$_6$In$_2$Te$_6$·4en (en is ethylenediamine) (Wang & Haushalter, 1997) and (NEt$_4$)$_5$[In$_3$Te$_7$]·0.5Et$_2$O (Park *et al.*, 1995)}; one-dimensional {[InTe$_2$]$^-$}$_n$ chains built up from InTe$_4$ tetrahedra sharing opposite edges in [(*n*-C$_4$H$_9$)$_4$N]$_2$[In$_2$Te$_4$] (Warren *et al.*, 1994) or [Zn(taa)-

(μ-tren)$_{0.5}$][InTe$_2$]Cl [taa is *N,N,N*-tris(2-aminoethyl)amine and tren is triethylenetetramine], [*M*(en)$_3$][In$_2$Te$_4$]·en (*M* = Ni or Co) and [*M*(en)$_3$]$_2$[In$_4$Te$_8$]·0.5en (*M* = Mn, Fe or Zn) (Zhou *et al.*, 2007); one-dimensional chains with fused five-membered rings in [*M*(en)$_3$][In$_2$Te$_6$] (*M* = Fe or Zn) and α- or β-[Mo$_3$(en)$_3$(μ_2-Te$_2$)$_3$(μ_3-Te)(μ_3-O)][In$_2$Te$_6$] (Li *et al.*, 1997); a two-dimensional layered network built of an In$_4$Te$_{10}$ super-tetrahedron sharing bonds *via* μ_2-Te, μ_2-Te$_2$ and μ_6-Te$_3$ in [Zn(en)$_3$]$_4$[In$_{16}$(Te$_2$)$_4$(Te$_3$)Te$_{22}$] (Chen *et al.*, 2001); and three-dimensional frameworks constructed from the crosslinking of helical chains of corner-sharing InTe$_4$ tetrahedra in UCR-2InTe-amine [amine = triethylenetetramine, tris(2-amino-ethyl)amine or *N*-(2-aminoethyl)propane-1,3-diamine; UCR-2InTe represents the [In$_{33}$Te$_{56}$]$^{13-}$ anion; UCR = University of California at Riverside] (Wang *et al.*, 2002). The cations of these compounds are tetraalkylammonium, protonated amine, alkali metal cations or transition metal complex cations, but indium tellurides with lanthanide-containing counter-cations prepared under mild solvothermal conditions are rare. The only example that has been found is [LaCl(en)$_4$][In$_2$Te$_4$], (II) (Chen *et al.*, 1998), which contains one-dimensional straight {[InTe$_2$]$^-$}$_n$ anion chains. We report here the unusual example of the title indium telluride, {[SmCl(en)$_4$][In$_2$Te$_4$]}$_n$, (I), containing sinusoidal {[InTe$_2$]$^-$}$_n$ anion chains with [SmCl(en)$_4$]$^{2+}$ as counter-ions.

(I)
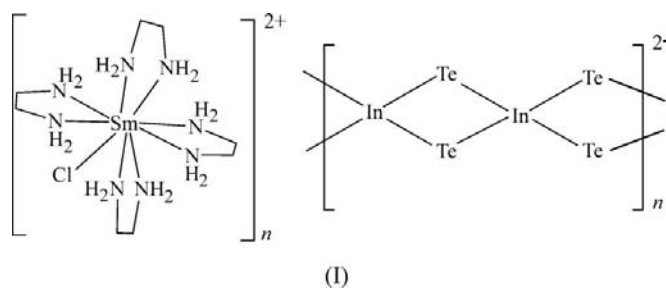
In the asymmetric unit of (I), there are two In atoms, one Sm atom and four Te atoms, all of which occupy general positions. The Sm^{III} centre is chelated by four bidentate en ligands and coordinated by one chloride ion to form a monocapped square-antiprismic geometry (Fig. 1*a*). The one-dimensional polymeric anion chain with the formula {[In$_2$Te$_4$]$^{2-}$}$_n$ is built of InTe$_4$ tetrahedra sharing opposite edges and propagates along the crystallographic *a* axis (Fig. 1*b*). All central In atoms in (I) are arranged in a sinu-soidal line and the In···In···In angles are in the range 157.04 (3)–160.81 (3)°. There are two kinds of In···In distances in (I), namely 3.6170 (11) Å for In1···In2 and 3.4948 (11) Å for In1···In2^{ii} [symmetry code: (ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$]. The repeat unit consists of four edge-sharing InTe$_4$ tetrahedra for a complete sinusoidal period of 13.7359 (11) Å, which is less than the sum of the four In···In distances [14.224 (2) Å]. The atoms in the In1/Te3/Te4/In2 ring are almost coplanar, but the In1/Te1/Te2/In2^{ii} ring has a butterfly structure; the dihe-dral angle between the wing planes In1/Te1/In2^{ii} and In1/Te2/In2^{ii} is 28.82 (4)°. When viewed down the one-dimensional
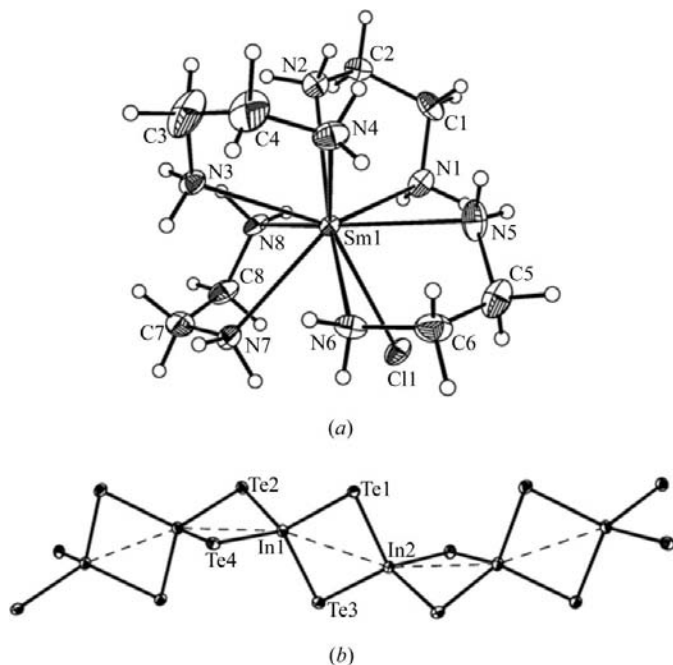
Figure 1
Views of (*a*) the cation and (*b*) the anion of (I), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Figure 2
A view of the structure of (I) along the [100] direction. All N—H···Cl contacts have been omitted for clarity.

Figure 3
Part of the crystal structure of (I), showing the N—H···Cl hydrogen bonds (dashed lines).

$\{[InTe_2]^-\}_n$ chain axis, the butterfly rings display two alternating orientations (Fig. 2). A search of the Cambridge Structural Database (Allen, 2002) reveals that this sinusoidal period is rather shorter than that observed in a number of en transition metal-containing indium tellurides (transition metal = Mn, Fe, Co, Ni or Zn; Zhou *et al.*, 2007), where it is in the range *ca* 14.2–14.6 Å.

In (I), $[SmCl(en)_4]^{2+}$ cations are linked into a one-dimensional sinusoidal cationic chain by way of N—H···Cl hydrogen bonds (Fig. 3) running parallel to the *a* axis. Pseudo-channels are constructed by the cationic chains surrounding the one-dimensional $\{[InTe_2]^-\}_n$ chains (Fig. 2).

Both (I) and the reported $[LaCl(en)_4][In_2Te_4]$, (II) (Chen *et al.*, 1998), contain a chloride ion which coordinates to the Ln^{III} centre to complete the coordination, but the role of this ion in the two structures is different. The $[SmCl(en)_4]^{2+}$ cations of (I) are assembled into a one-dimensional sinusoidal chain by N—H···Cl hydrogen bonds but, importantly, no similar hydrogen bonds exist between the $[LaCl(en)_4]^{2+}$ cations of (II). The ionic radius of the Sm^{3+} ion (1.132 Å) (Suganuma & Hori, 1999) is smaller than that of the La^{3+} ion (1.216 Å) (Lien *et al.*, 2005). When the chloride ion bonds to the Sm^{3+} ion of (I), its bond [2.869 (3) Å] is shorter than the La—Cl bond in (II) [2.945 (9) Å], and the electronegativity of the Cl atom in (I) should be higher than that in (II). For an N—H···Cl hydrogen bond, it is well known that the higher the electronegativity of the Cl acceptor, the stronger the hydrogen bond. Thus, the hydrogen-bond-assembled sinusoidal cation chain in (I) affects the conformation of the anion. There is no such templating effect in (II) and the anionic chains are therefore straight and thus (I) and (II) show different conformations of the polymeric anions.
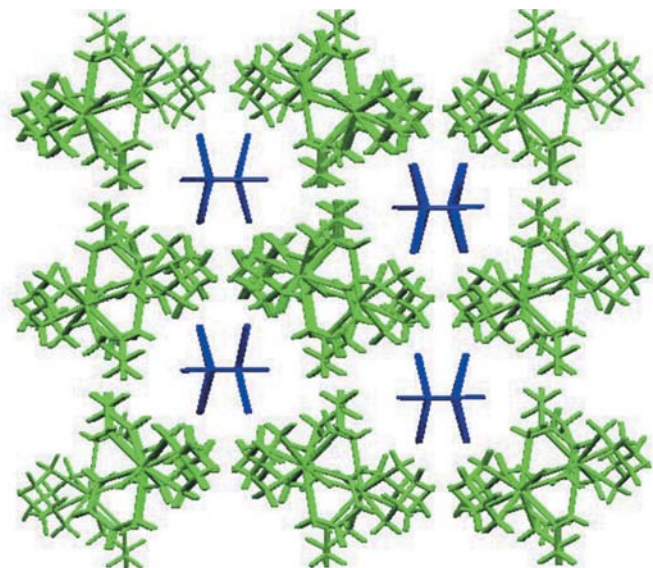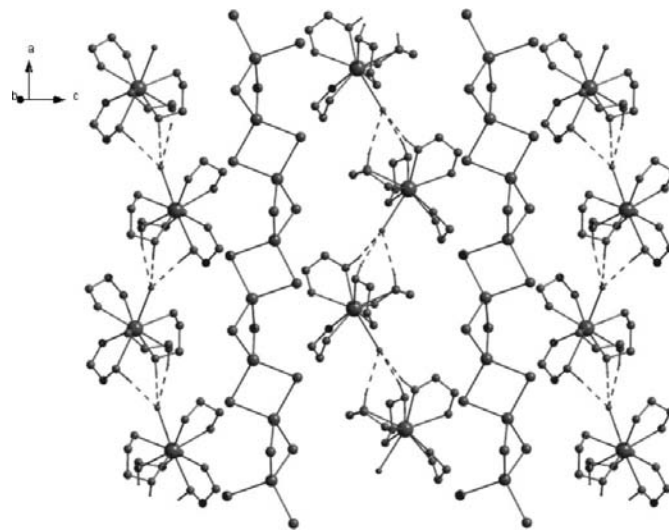
Experimental

Single crystals of the title complex suitable for X-ray crystallographic analysis were obtained by solvothermal treatment of SmCl$_3$ (0.05 mmol), InCl$_3$ (0.1 mmol), Te powder (0.2 mmol) and ethylenediamine (1 ml). The reagents were placed in a thick sealed Pyrex tube (*ca* 20 cm long), which was heated to 418 K for 13 d and then cooled to room temperature. Yellow block-shaped crystals of (I) were obtained (yield 26%, based on Sm).

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Table 1
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$N2—H2A\cdots Cl1^i$	0.91	2.74	3.619 (10)	164
$N3—H3A\cdots Cl1^i$	0.91	2.40	3.248 (10)	156
$N8—H8A\cdots Cl1^i$	0.91	2.60	3.498 (9)	169
$N7—H7A\cdots Cl1$	0.91	2.72	3.166 (10)	111

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 Å and N—H = 0.91 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$. There was some evidence of disorder in the en ligand containing atoms N3 and N4. This was refined with geometric and displacement parameter restraints to improve the geometry using a single set of atom positions. Rigid-bond and similarity restraints were applied to the displacement parameters of atoms N3/C3/C4/N4 of one chelating ligand. This ligand was restrained to have twofold symmetry and to have a geometry similar to that of the N1/C1/C2/N2 ligand.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008);

molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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