

# Template synthesis of $[\text{Cr}(\text{en})_3][\text{Te}_6]$ : a novel polytelluride with a framework structure, whose cavities are filled with a $[\text{Cr}(\text{en})_3]^{3+}$ template

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**$[\text{Cr}(\text{en})_3][\text{Te}_6]$  (en = ethylenediamine) is obtained by a template synthesis under solvothermal conditions from  $\text{Cr}(\text{CO})_6$  and  $\text{BaTe}_4$ ; its crystal structure contains a polymeric  $\text{Te}_6^{3-}$  framework whose pores contain the  $[\text{Cr}(\text{en})_3]^{3+}$  template;  $[\text{Cr}(\text{en})_3][\text{Te}_6]$  is the first chalcogenide with a porous three-dimensional framework structure.**

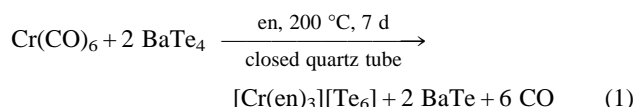
Microporous materials with a three-dimensional framework of condensed  $\text{MO}_4$  tetrahedra ( $M = \text{e.g. Al, Si, P}$ ) have been known for a long time as zeolites. They have great technical importance as molecular sieves and catalysts.<sup>1,2</sup> Their sorptive properties are based on the regular arrangement of cavities with defined diameter and size, which can be varied by the use of templates.<sup>3</sup> On the other hand, the complexing properties of compounds with porous structures can be used for the stabilisation of various cluster species (e.g.  $\text{Cd}_m\text{S}_n$  or  $\text{Si}_8$ ).<sup>4</sup>

Recent examples of Si- or Al-free compounds with microporous structures based on tetrahedral building elements have been found in the gallophosphate cloverit, whose cavities are formed from twenty-membered rings,<sup>5</sup> in the nitridophosphate  $\text{Zn}_7[\text{P}_{12}\text{N}_{24}]\text{Cl}_2$ <sup>6</sup> and in several transition-metal phosphates.<sup>7</sup> The substitution of tetrahedral structure motifs in known aluminosilicates by octahedral or by square-pyramidal  $\text{MO}_n$  building groups in early transition-metal phosphates opens the way to a new and versatile structural chemistry.<sup>8</sup> A nice example, the  $[\text{V}_{10}\text{O}_{10}(\text{H}_2\text{O})_2(\text{OH})_4(\text{PO}_4)_7]^{6-}$  polyanion, which can be synthesized by self-assembly from simple reagents and whose structure can be viewed as an inorganic double helix built from vanadium phosphate units, has recently been reported by Haushalter *et al.*<sup>9</sup>

Except for a few examples, all compounds with porous structures are oxidic. This explains their thermal stability and insulating electrical properties. On the other hand, metal chalcogenides (e.g.  $\text{CuInS}_2$ ,  $\text{MnQ}$ ,  $\text{CdQ}$ ;  $\text{Q} = \text{S, Se, Te}$ ) are important materials for electronic devices because of their magnetic or semiconducting properties.<sup>10</sup> Sulfides possess enormous compositional and structural variety.<sup>11,12</sup> Therefore, in view of the utility of microporous oxides in chemical catalysis and the wide applicability of chalcogenides in electronic devices a new class of compounds with a combination of the properties of zeolitic and sulfidic materials should be an attractive synthetic target. Solvothermal methods or reactive flux methods are possible preparative routes to these new materials.<sup>†</sup> Sheldrick and Braunbeck have described the solvothermal synthesis of chalcogenostannates.<sup>13</sup> Dhingra and Kanatzidis obtained  $[\text{PPh}_4][\text{M}(\text{Se}_6)_2]$ , a compound with an open-layer structure by reacting gallium, indium and thallium with low-melting polychalcogenide fluxes.<sup>14</sup> Herein we report the synthesis and characterization of  $[\text{Cr}(\text{en})_3][\text{Te}_6]$  **1** whose structure is built up from a polytelluride framework with pores filled by templating  $[\text{Cr}(\text{en})_3]^{3+}$  ions.

The title compound was first obtained by the reaction of  $\text{Cr}(\text{CO})_6$  with an alloy of the nominal composition  $\text{BaAs}_4\text{Te}_4$ . Based on the assumption that reactions of polytellurides with hard 3d metal cations (e.g.  $\text{Cr}^{3+}$  or  $\text{Mn}^{2+}$ ) only lead to products with isolated oligotelluride anions  $\text{Te}_n^{2-}$  ( $n = 2, 3$ ) and  $[\text{M}(\text{en})_3]^{m+}$  ( $m = 2, 3$ ), the initial target was the assembly of a

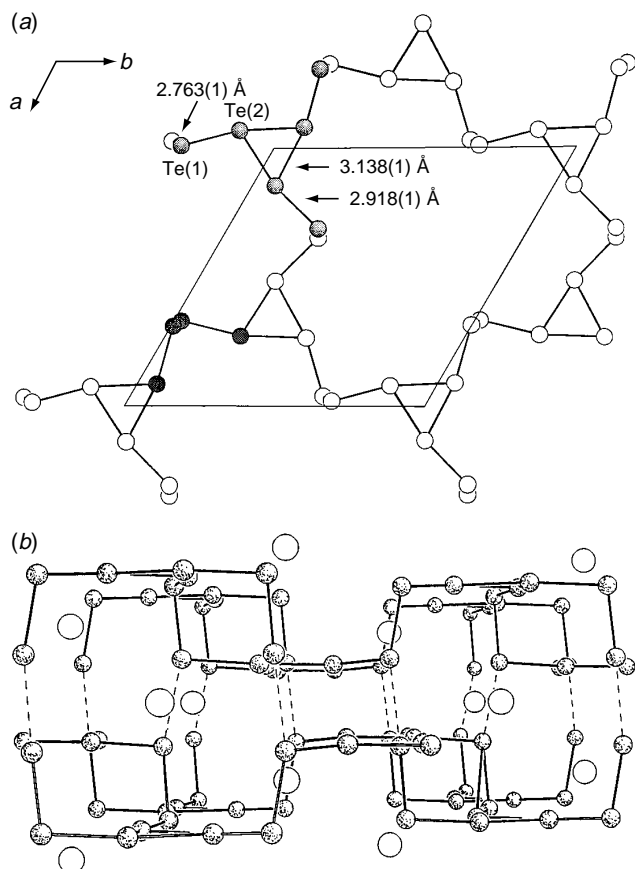
framework structure with bridging  $\text{AsTe}_n$  ( $n = 3, 4$ ) elements stabilized by templating  $[\text{Cr}(\text{en})_3]^{3+}$  cations which are formed by oxidative decarbonylation of  $\text{Cr}(\text{CO})_6$ .<sup>15</sup> Further investigations and the results of the X-ray analysis revealed that **1** represents the crystalline part of the reaction products.<sup>‡</sup> It can also be prepared by the reaction of  $\text{Cr}(\text{CO})_6$  with a melt of nominal composition  $\text{BaTe}_4$  [eqn. (1)].<sup>§</sup>



Whereas reaction of the educts in boiling en under normal pressure yields powder-like products, the combination of the reaction with  $\text{Te}_x^{2-}$  polytellurides as mineralizers leads to well crystallized products. **1** was removed from the reaction mixture by crystallization and should be the kinetically stable reaction product. The homogeneity of the product was confirmed from Guinier powder data.

The structure of **1** contains a polymeric  $[\text{Te}_6]^{3-}$  polyanion,<sup>16</sup> whose pores are filled by isolated octahedrally coordinated  $[\text{Cr}(\text{en})_3]^{3+}$  cations. The characteristic structural features of the  $\text{Te}_6^{3-}$  polyanion are puckered sheets of Te atoms parallel to the *ab*-plane which are shown in Fig. 1(a) in a projection along [001]. Fig. 1(b) shows a view of the structure along [100]. Each of these sheets is made up from  $\text{Te}_6$  fragments which are linked to each other by Te–Te single bonds [ $d_{\text{Te–Te}} = 2.763(1) \text{ \AA}$ ]. The  $\text{Te}_6$  fragments contain a central  $\text{Te}_3$  ring with one exocyclic Te atom bonded to each atom of the ring. The Te–Te distances of  $3.138(1) \text{ \AA}$  within the ring are approximately  $0.3 \text{ \AA}$  longer than a typical Te–Te single bond distance ( $2.84 \text{ \AA}$  in the structure of elemental tellurium<sup>17</sup>). A formal bond order of 0.32 can be calculated using Paulings's rule [ $d(n) = d(1) - 0.61 \log(n)$ ,  $d(1) = 2.796 \text{ \AA}$ ].<sup>18</sup> The exocyclic Te–Te separations of  $2.918(1) \text{ \AA}$  are approximately  $0.2 \text{ \AA}$  longer than typical Te–Te bond distances in polytellurides (e.g.  $d_{\text{Te–Te}} = 2.726 \text{ \AA}$  in  $\text{Te}_4^{2-}$ <sup>19</sup>), but they are comparable with the Te–Te distances in  $\text{Te}_2$  units encountered in the structures of  $\text{K}_4\text{M}_3\text{Te}_{17}$  ( $M = \text{Zr, Hf}$ ).<sup>20</sup> The shortest Te–Te distances of  $3.376(1) \text{ \AA}$  between the layers are much shorter than the sum of the van der Waals radii of  $4.4 \text{ \AA}$ <sup>19</sup> and comparable with the Te–Te distances in the polytelluride cluster  $[\text{NbTe}_{10}]^{3-}$ .<sup>21</sup> According to the results of an MO study these values correspond to significant Te–Te bonding interaction.<sup>22</sup> The computed Pauling bond order is 0.11. Therefore, the Te sheets in the structure of **1** should not be viewed as isolated layers.

An alternative description may be given based on the hierarchy of the bonding. (i) Considering only distances in the range of  $2.7 \text{ \AA}$  to  $3.0 \text{ \AA}$  as bonding, the structure consists of isolated  $\text{Te}_4^{2-}$  chains. This description is in accord with conventional bonding considerations in polychalcogenides. However, the presence of additional partially bonding Te–Te bonding interactions indicates that this description does not allow to fully understand the bonding situation in the  $\text{Te}_6^{3-}$  polyanion. (ii) Alternatively, if we consider all Te–Te distances shorter than  $3.15 \text{ \AA}$  as bonding, a puckered layer structure with  $\text{Te}_6$  motifs linked by Te–Te single bonds ( $d_{\text{Te–Te}} = 2.763 \text{ \AA}$ ) is



**Fig. 1** (a) Structure of the  $\text{Te}_6^{3-}$  polyanion depicted in a view along [001]. (b) Two Te layers in a view along [100]. The positions of the  $\text{Cr}(\text{en})_3^{3+}$  cations are indicated by open spheres.

found [see Fig. 1(a)]. (iii) Counting all Te–Te distances shorter than 3.4 Å as bonding leads to a three-dimensional framework structure with pores containing solvated  $\text{Cr}(\text{en})_3^{3+}$  cations ( $\Delta$  and  $\Delta$  isomer, two crystallographically independent cations per unit cell). **1** is air-stable for several weeks. Thermal decomposition starts at 200 °C and is complete at 280 °C. Above 360 °C **1** transforms to other still uncharacterized products.

Although the electronic reasons for the stability of **1** can be rationalized by qualitative MO arguments, the mechanism of its formation is still unclear. The templating properties of the highly charged  $\text{Cr}(\text{en})_3^{3+}$  seems to be essential for the synthesis of **1**. Attempts to synthesize other related compounds with various  $\text{M}(\text{en})_3^{2+}$  cations ( $\text{M}$  = alkaline earth or 3d metal) only yield known chain-like polytellurides. The synthesis of further polytellurides with porous structures by means of coordinating ligands and highly charged cations is currently under investigation.

#### Footnotes

† This corresponds to the formation conditions of naturally occurring sulfidic minerals.

‡ *Crystal data* for  $[\text{Cr}(\text{en})_3][\text{Te}_6]$ :  $\text{C}_6\text{H}_{12}\text{CrN}_6\text{Te}_6$ ,  $M = 985.8$ , trigonal, space group  $R\bar{3}2$  (no. 155),  $Z = 6$ ,  $a = 14.292(2)$ ,  $b = 14.292(2)$ ,  $c = 18.076(3)$  Å,  $U = 3197.56$  Å<sup>3</sup>,  $D_c = 1.536$  g cm<sup>-3</sup>. Siemens P4, MoK $\alpha$ ,  $\mu = 8.58$  mm<sup>-1</sup>, crystal size 0.15 × 0.15 × 0.15 mm,  $\theta$ –2 $\theta$  scan,  $2\theta_{\text{max}} = 54^\circ$ , 5446 reflections collected, 1564 independent reflections, 1485 reflections with  $I > 2\sigma(I)$ ,  $R(R_w) = 0.021(0.021)$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/337.

§  $[\text{Cr}(\text{en})_3][\text{Te}_6]$ : 44 mg of  $\text{Cr}(\text{CO})_6$  (0.2 mmol) and 259 mg of an alloy with the nominal composition  $\text{BaTe}_4$  were loaded into a quartz tube (volume ca. 20 ml). After introducing 2 ml of en, the tube was sealed under vacuum (ca.  $10^{-3}$  bar). After 7 days of heating at 200 °C, the tube was cooled at 1 °C min<sup>-1</sup> and opened. Black cubic crystals could be isolated from the colourless solution. The crystals were washed with tetrahydrofuran and dried *in vacuo*. Yield: 127 mg (63.3%), satisfactory elemental analysis, IR data: (KBr pellet) 3397m, 3480m, 3030s, 2912s, 2870s, 1547s, 1447s cm<sup>-1</sup>.

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