inorganic papers

Tetratellurium bis[heptachlorodigallate(III)], $Te_4[Ga_2Cl_7]_2$

Martin Lindsjö* and Lars Kloo

Royal Institute of Technology, Division of Inorganic Chemistry, S-10044 Stockholm, Sweden

Correspondence e-mail: martin@munin.inorg.kth.se

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(e–Te) = 0.001 Å
R factor = 0.032
wR factor = 0.060
Data-to-parameter ratio = 30.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

$Te_4[Ga_2Cl_7]_2$ has been isolated from $GaCl_3$–benzene media and its structure determined. The structure features a centrosymmetric square-planar Te_4^{2+} cation and staggered $[Ga_2Cl_7]^-$ anions, consisting of two corner-sharing $GaCl_4$ tetrahedra. The chlorine bridge between the Ga atoms in the anion is bent. The title compound is isotypic with $Te_4[Al_2Cl_7]_2$.

Comment

Much attention has been paid to the coloured solutions produced when elemental chalcogens are dissolved in strongly acidic media. It has become well known that this coloration is caused by the formation of polycationic species, and a large number of compounds containing such chalcogen polycations have been isolated from routes employing molten salts, superacidic media or chemical vapour transport synthetic methods (Beck, 1997; Brownridge *et al.*, 2000). Meanwhile, we have recently described an alternative procedure for the synthesis of bismuth polycations, using solutions of $GaCl_3$ in benzene (Ulvenlund *et al.*, 1995; Lindsjö *et al.*, 2005). It has been expected that this synthetic route could be extended to other groups of the periodic table. We report here the structure of $Te_4[Ga_2Cl_7]_2$, (I), the first compound containing a chalcogen polycation isolated by this route.

When tellurium powder is dissolved in a $GaCl_3$–benzene medium, a green solution is produced. By methods described in detail in our earlier work (Lindsjö *et al.*, 2005), single crystals of (I) can be isolated. The structure of (I) is isotypic with that of $Te_4[Al_2Cl_7]_2$, obtained from a molten $AlCl_3$ medium (Couch *et al.*, 1972), and features an almost ideal square-planar Te_4^{2+} cation lying on an inversion centre. The anion consists of two corner-sharing tetrahedra, with a bent chlorine bridge between the two Ga atoms. The conformation of the $[Ga_2Cl_7]^-$ anion is staggered (Fig. 1).

As noted previously for the aluminate structure, some of the Cl atoms are positioned in the plane of the cation, capping the edges of these. These contacts constitute the shortest
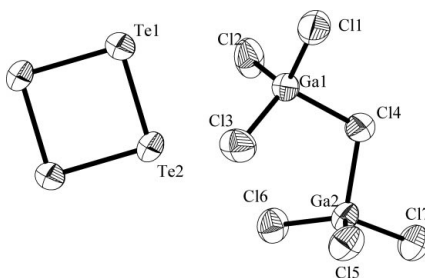

Figure 1
The cation and anion of (I), displaying displacement ellipsoids at the 70% probability level. Unlabelled Te atoms are related to Te1 and Te2 by the inversion operator $(1 - x, -y, -z)$.

Te···Cl distances of the structure, ranging from 3.277 (3) to 3.506 (4) Å (Fig. 2).

In the Raman spectrum of (I), bands are observed at 427 (*w*), 365 (*m*) and 213 cm^{-1} (*s*). In agreement with the characterized structure, the two bands at higher wavenumbers can be attributed to the $[Ga_2Cl_7]^-$ anion (Grodzicki & Potier, 1973), while the peak at 213 cm^{-1} is observed as the strongest band of the Te_4^{2+} polycation (Burns & Gillespie, 1982).

Experimental

GaCl$_3$ (0.30 g, 1.7 mmol) was dissolved in benzene (0.5 ml) and Te powder (0.051 g, 0.40 mmol) was added. After a couple of hours, the solution was dark green in colour. Crystals of (I) were obtained by first adding an overlayer of hexane on top of the green solution, and then, after 24 h, removing the hexane and instead adding mesitylene. A small quantity of black block-shaped crystals formed near the phase border after a few days.

Crystal data

Te$_4$[Ga$_2$Cl$_7$]$_2$	$D_x = 3.236$ Mg m^{-3}
$M_r = 1285.62$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 116
$a = 9.1244$ (6) Å	reflections
$b = 11.0468$ (7) Å	$\theta = 4.3$–20.7°
$c = 13.0895$ (7) Å	$\mu = 9.78$ mm^{-1}
$\beta = 90.152$ (6)°	$T = 296$ K
$V = 1319.36$ (14) Å^3	Block, black
$Z = 2$	$0.25 \times 0.25 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer	3013 independent reflections
φ and ω scans	2350 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.063$
(*HABITUS*; Herrendorf &	$\theta_{max} = 27.5°$
Bärnighausen, 1997)	$h = -11 \rightarrow 10$
$T_{min} = 0.111$, $T_{max} = 0.159$	$k = -14 \rightarrow 14$
16 007 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0088P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 3.3218P]$
$wR(F^2) = 0.060$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
3013 reflections	$\Delta\rho_{max} = 0.58$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -0.94$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

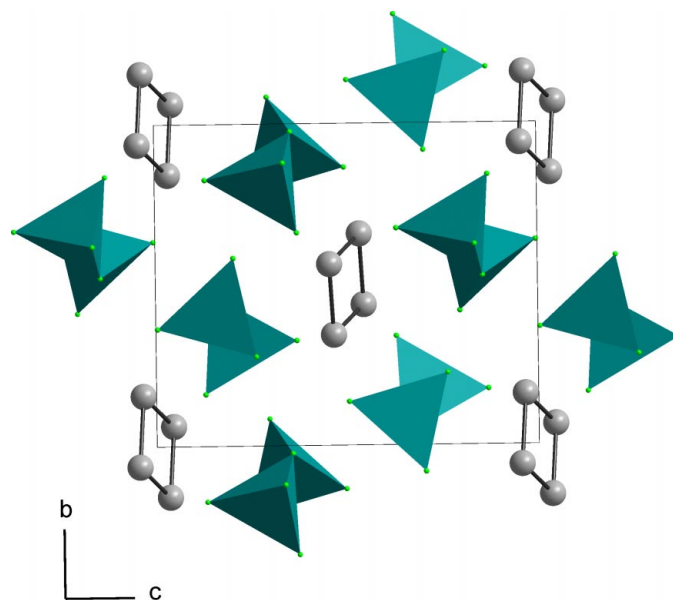|			
Te1—Te2^i	2.6571 (5)	Ga1—Cl4	2.2835 (14)
Te1—Te2	2.6608 (5)	Ga2—Cl4	2.2990 (14)
Ga1—Cl1	2.1269 (15)	Ga2—Cl5	2.1504 (15)
Ga1—Cl2	2.1490 (16)	Ga2—Cl6	2.1260 (14)
Ga1—Cl3	2.1293 (16)	Ga2—Cl7	2.1289 (15)
Te2^i—Te1—Te2	89.999 (15)	Cl6—Ga2—Cl5	117.44 (6)
Cl1—Ga1—Cl2	114.74 (7)	Cl7—Ga2—Cl4	101.43 (6)
Cl1—Ga1—Cl3	114.43 (7)	Cl7—Ga2—Cl5	110.84 (7)
Cl1—Ga1—Cl4	104.93 (6)	Ga1—Cl4—Ga2	108.89 (6)

Symmetry code: (i) $1 - x, -y, -z$.

Figure 2
Packing diagram of (I), viewed down the crystallographic *a* axis. The $[Ga_2Cl_7]^-$ anions are shown as polyhedra.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

References

Beck, J. (1997). *Coord. Chem. Rev.* **163**, 55–70.
Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Brownridge, S., Krossing, I., Passmore, J., Jenkins, H. D. B. & Roobottom, H. K. (2000). *Coord. Chem. Rev.* **197**, 397–481.
Burns, R. C. & Gillespie, R. J. (1982). *Inorg. Chem.* **21**, 3877.
Couch, T. W., Lokken, D. A. & Corbett, J. D. (1972). *Inorg. Chem.* **11**, 357–362.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Grodzicki, A. & Potier, A. (1973). *J. Inorg. Nucl. Chem.* **35**, 61–66.
Herrendorf, W. & Bärnighausen H. (1997). *HABITUS*. Universities of Karlsruhe and Gießen, Germany.
Lindsjö, M., Fischer, A. & Kloo, L. (2005). *Eur. J. Inorg. Chem.* In the press.
Mackay, S., Gilmore, C. J., Edwards, C., Stewart, N. & Shankland, K. (1999). *maXus*. Nonius BV, The Netherlands, MacScience, Japan, and The University of Glasgow, Scotland.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Ulvenlund, S., Wheatley, A. & Bengtsson, L. A. (1995). *J. Chem. Soc. Chem. Commun.* pp. 59–60.