A new modification of thallium chromate related to the β-K$_2$SO$_4$ family

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The title structure is a new modification of Tl$_2$CrO$_4$. There are four independent Tl$^+$ cations and two [CrO$_4$]$^{2-}$ anions in the structure. It is closely related to the already known modification, which belongs to the β-K$_2$SO$_4$ family with two independent cations and one anion. In both modifications, the cations and anions are situated on crystallographic mirror planes. The volume of the asymmetric unit of the title structure is ~0.4% smaller than that of the known modification belonging to the β-K$_2$SO$_4$ family. The other difference between the two modifications is seen in the environment of the cations. In the title structure, none of the Tl$^+$ cations is underbonded, in contrast with the modification isostructural with β-K$_2$SO$_4$. In the β-K$_2$SO$_4$ family with simple cations, underbonding of one of the constituent cations is typical. The dependence of the unit-cell parameters on temperature does not indicate a phase transition in the interval 90–300 K.

Comment

The aim of the present work was the growth of single crystals of Tl$_2$CrO$_4$ of the known modification belonging to the β-K$_2$SO$_4$ family. Spectroscopic experiments were planned for these samples. Moreover, the previous structure determination of Tl$_2$CrO$_4$ (Carter & Margulis, 1972) does not meet current standards: R_{obs} = 0.07, and some structural features deviate slightly from the trends in the β-K$_2$SO$_4$ family (see below and Table 1). Therefore, we also aimed to carry out a new single-crystal X-ray structure determination of the compound. As a result of our experiment, a new modification of Tl$_2$CrO$_4$ has been prepared, the structure of which is presented and discussed here.

Tl$_2$SeO$_4$ (Fábry & Breczewski, 1993; Friese *et al.*, 2004), Tl$_2$CrO$_4$ (Carter & Margulis, 1972), K$_2$SeO$_4$ (see, for example, González-Silgo *et al.*, 1996) and K$_2$CrO$_4$ (Toriumi & Saito, 1978) are isostructural compounds belonging to the β-K$_2$SO$_4$ family, a structural family characterized by its variety of low-temperature phase transitions. Thus, K$_2$SeO$_4$ and Tl$_2$SeO$_4$ are known to undergo low-temperature phase transitions, while K$_2$CrO$_4$ and Tl$_2$CrO$_4$ do not (Fábry & Pérez-Mato, 1994).

Tl$_2$SeO$_4$, a compound chemically and structurally closely related to the title structure, is exceptional among the members of the β-K$_2$SO$_4$ family because it undergoes a unique sequence of phase transitions during cooling. A second-order phase transition takes place at 97 K (Matsuo & Ikehata, 2004), followed by a first-order low-temperature phase transition at about 72 K (Grunwald *et al.*, 1984a,b). The latter phase transition is accompanied by a change in symmetry from *Pnma* to $P2_12_12_1$ without multiplication of the number of formula units in the unit cell (see, for example, Friese *et al.*, 2004). A reverse phase transition during heating takes place at 76 K (Matsuo *et al.*, 2000; Matsuo & Ikehata, 2004). In other members of this structural family, a sequence of phase transitions often takes place from the incommensurately modulated to commensurately modulated phases on lowering the temperature.

The difference between Tl$_2$SeO$_4$ and the other members of the β-K$_2$SO$_4$ family may be related to the extreme underbonding (Table 1) of one of the two independent cations that are present in this structural type. This underbonding is quite common in the members of the β-K$_2$SO$_4$ family. In the case of Tl$_2$SeO$_4$, however, and to a lesser extent in Tl$_2$CrO$_4$ (Carter & Margulis, 1972), this underbonding is quite prominent (Fábry & Pérez-Mato, 1994). It is interesting that this underbonded cation is often bonded by quite a short cation–anion bond, often the shortest in the structure (Fábry & Pérez-Mato, 1994). This holds for, among others, the structures of Tl$_2$SeO$_4$ (Fábry & Breczewski, 1993; Friese *et al.*, 2004), Tl$_2$CrO$_4$ (Carter & Margulis, 1972) and K$_2$SeO$_4$ (González-Silgo *et al.*, 1996).

Although the respective cations in Tl$_2$CrO$_4$ and K$_2$CrO$_4$ are underbonded, low-temperature phase transitions are not known, in contrast with Tl$_2$SeO$_4$ and K$_2$SeO$_4$ (González-Silgo *et al.*, 1996). However, spectroscopic measurements indicated a pretransitional phenomenon in K$_2$CrO$_4$, *i.e.* an incomplete mode softening (Etxebarría *et al.*, 1992). It cannot be excluded that a similar pretransitional phenomenon may occur in Tl$_2$CrO$_4$.

The unit-cell volume of the title polymorph is almost exactly doubled compared with the known polymorph described by Carter & Margulis (1972). The volumes of the asymmetric units in the title structure and in the β-K$_2$SO$_4$ polymorph are 124.88 and 125.37 Å^3, respectively. There are four independent Tl$^+$ cations and two [CrO$_4$]$^{2-}$ anions in the title structure, in contrast with the presence of two independent cations and one anion in the β-K$_2$SO$_4$ polymorph. Nevertheless, both modifications of Tl$_2$CrO$_4$ show similar structural features. The constituent cations and anions are situated on the crystallographic mirror planes in the two polymorphs. The transformation of the lattice parameters of the β-K$_2$SO$_4$ modification (o index), $[a_m,b_m,c_m] = [/0\ \bar{1}\ \bar{1}/1\ 0\ 0/0\ 0\ 2/]\ [a_o,b_o,c_o]$, leads to a unit cell similar to that of the title structure (m index). ($[a_m,b_m,c_m]$ and $[a_o,b_o,c_o]$ are the column matrices, while /0 $\bar{1}$ $\bar{1}$/, /1 0 0/ and /0 0 2/ are the first, second and third rows, respectively, of the 3 × 3 matrix.) The transformed unit-cell
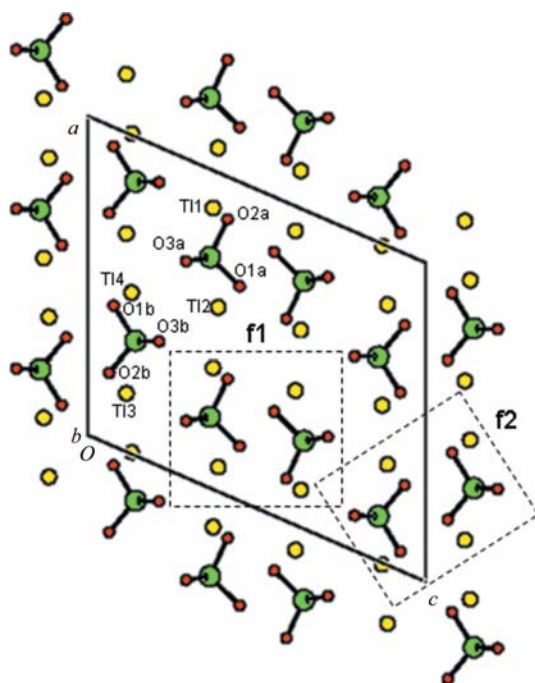
Figure 1
A view of the unit cell of the title structure of Tl_2CrO_4 along the monoclinic axis. The dashed-line boxes indicate similar environments for the cations, *cf.* Fig. 2.
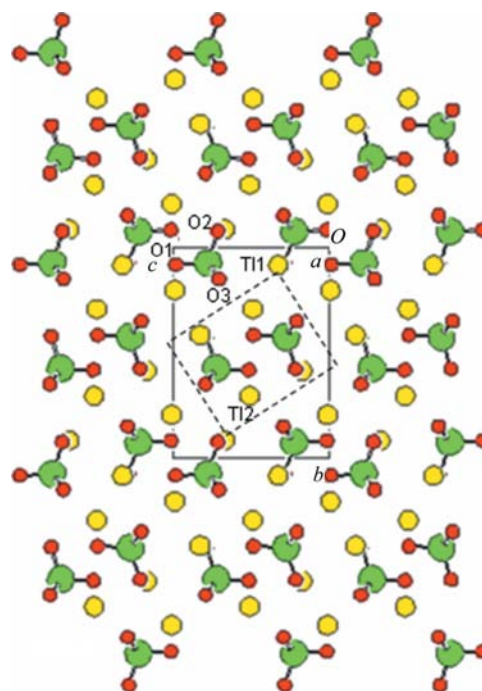
Figure 2
A view of the β-K_2SO_4 polymorph of Tl_2CrO_4 along the *a* axis [setting *Pmcn*, as given by Carter & Margulis (1972)], *cf.* Fig. 1.

parameters are 13.328 (5), 5.910 (4) and 15.820 (8) Å, 90, 126.40 (3) and 90°, and $V = 1003$ (1) $Å^3$.

Fig. 1 shows the packing of the constituents in the unit cell of the title structure when viewed along the unit-cell *b* axis. Fig. 2 shows a view of the β-K_2SO_4 polymorph (Carter & Margulis, 1972), also perpendicular to the mirror plane *m*, using the original unit-cell setting *Pmcn*. It can be seen from Fig. 1 that the cation pairs Tl1/Tl2 and Tl3/Tl4 are situated along planes parallel to (001); the former pairs are situated at approximately $z = \frac{1}{2}$ and the latter pairs at approximately $z = 0$. The arrangements within the sections in the title structure and the β-K_2SO_4 polymorph show similarities that are depicted by dashed-line boxes in the figures.

Cations Tl1, Tl2, Tl3 and Tl4 are surrounded by eight, nine, nine and eight O atoms, respectively (Figs. 3 and 4), within a distance of 4.0 Å. In fact, the longest Tl—O distance among the coordinated O atoms in the title structure is 3.402 (12) Å for Tl1—O1$(x + \frac{1}{2}, y + \frac{1}{2}, z)$. The coordination numbers (CN) in the title structure are on average lower than in the β-K_2SO_4 polymorph, where the CN up to 3.5 Å is 9 for both cations, and 11 and 9, respectively, up to 4.0 Å. Comparing the two polymorphs, the cations are more equally coordinated in the title structure. In both polymorphs, neighbouring cationic polyhedra around the Tl^+ cation pairs share a plane in most cases (Tables 2 and 3), although in the title structure the polyhedra are also shared by the edges.

A comparison of the bond-valence sums (BVS) in the title structure with those of related structures is given in Table 1. The cation BVS are much closer to each other than in the β-K_2SO_4 polymorph of Tl_2CrO_4 (Carter & Margulis, 1972), where one of the cations is underbonded while the other is

bound significantly more firmly. This is a tendency observed elsewhere in the β-K_2SO_4 structural family (Fábry & Pérez-Mato, 1994).

In the title structure, the relative contributions of the bond valence pertinent to the shortest $Tl^+—O^{2-}$ contact within the coordination environments of each of the Tl1, Tl2, Tl3 and Tl4 cations are 0.166 (8), 0.189 (5), 0.268 (8) and 0.196 (5), respectively. In the case of Tl3, the highest bond valence [0.308 (9)] corresponds to the shortest cation–anion bond in the structure, which is 2.608 (11) Å. On the other hand, in the β-K_2SO_4 polymorph (Carter & Margulis, 1972), the shortest $Tl^+—O^{2-}$ contacts were determined as 2.70 (9) (11-oxygen coordinated Tl) and 2.71 (8) Å (nine-oxygen coordinated Tl), with relative contributions of the respective bond valences of 0.28 (7) and 0.18 (4). However, by analogy with Tl_2SeO_4 (Friese *et al.*, 2004; Fábry & Breczewski, 1993), it can be expected that the former distance should be somewhat shorter and the latter longer.

It is difficult to predict which of the two modifications of Tl_2CrO_4 is thermodynamically more stable. The somewhat smaller unit-cell volume of the title structure indicates that it should be rather more stable than its β-K_2SO_4 polymorph. Also, the distribution of the cation BVS in the title structure, where not all the cations are underbonded, rather supports the view that it may be more stable than the modification isostructural with β-K_2SO_4. Also, the fact that, in the title structure, some of the anionic polyhedra are interconnected by the edges, and not by the faces, would enhance the probability that it would relax without abrupt changes on cooling (Tables 2 and 3). The low-temperature phase transition in closely related Tl_2SeO_4 (Table 1) causes a decrease in the CN
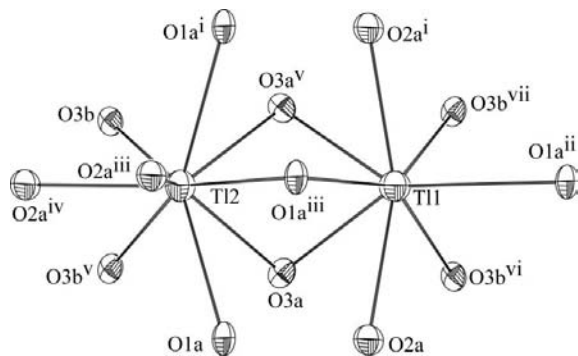
Figure 3
A view of the environment around atoms Tl1 and Tl2. The distance between Tl1 and Tl2 is 3.9772 (15) Å. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, 1 + y, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, 1 - z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} + y, z$; (v) $x, 1 - y, z$; (vi) $\frac{1}{2} + x, -\frac{1}{2} + y, z$; (vii) $\frac{1}{2} + x, \frac{3}{2} - y, z$.]
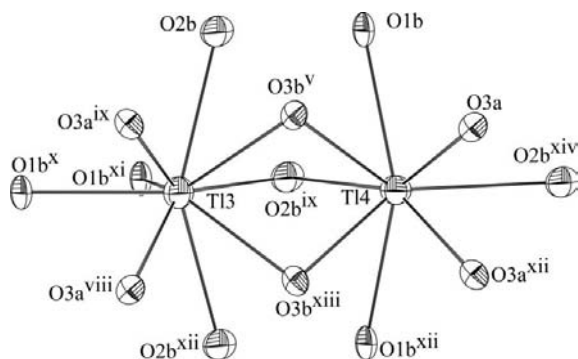

Figure 4
A view of the environment around atoms Tl3 and Tl4. The distance between Tl1 and Tl2 is 4.0127 (14) Å. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: as for Fig. 3. In addition: (viii) $-\frac{1}{2} + x, -\frac{1}{2} + y, -z$; (ix) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (x) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (xi) $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (xii) $x, -y, z$; (xiii) $x, -1 + y, z$; (xiv) $\frac{1}{2} + x, \frac{1}{2} - y, z$.]

of the cations from 11 to 10 and from 9 to 8 (up to 4.0 Å from the central cation), i.e. the situation is similar in this respect to the title structure. It is also of interest that, in the title structure, there are significantly and unusually underbonded O atoms, viz. O1a and O2b (Table 1). The dependence of the lattice parameters on temperature in the interval 90–300 K did not indicate a phase transition. (The scan was performed in 10 K intervals.) The differential scanning calorimetry experiments did not reveal a low-temperature phase transition either. However, the latter sample could contain the β-K$_2$SO$_4$ polymorph as well, since the temperatures pertinent to the high-temperature phase transition during heating and cooling corresponded well with the experiments carried out by Natarajan & Secco (1974).

The chemical strains GII (global instability indices) of some related compounds (Brown, 2005; Table 1) do not permit any definite conclusion about the structural stability of the title structure compared with the β-K$_2$SO$_4$ polymorph. This is partly due to the fact that, in most cases, there are both over- and underbonded cations in the β-K$_2$SO$_4$ structures (such as

Tl$_2$SeO$_4$), while it has been shown that precisely the underbonding of one of the constituent cations is related to the structural stability (Fábry & Pérez-Mato, 1994). The low-temperature phase transitions cause an increase in the BVS of both cations, though mostly the underbonded ones. Thus, the GII are not sensitive for this structural group. For example, the GII of the low-temperature phase of K$_2$SeO$_4$ (Yamada et al., 1984) is 0.212 (24), which is larger than that of the room-temperature phase of K$_2$SeO$_4$ [0.161 (10)] (Table 1). The other reason for the lower sensitivity of the GII in this case is due to the lower reliability of structure determinations of compounds with heavy cations such as Tl$^+$, which cause severe absorption at commonly used radiation wavelengths.

Experimental

Tl$_2$CrO$_4$ cannot be prepared by simply mixing aqueous solutions of suitable salts, since it is scarcely soluble: $K_p = 8.67 \times 10^{-13}$ (CRC Handbook of Chemistry and Physics, 2009). The title structure was prepared by a similar procedure to that described by Carter & Margulis (1972), although they used silica gel, which is different to the present preparation. The title crystals were prepared by the reaction of TlNO$_3$, previously dispersed in a gel formed by hydrolysis of tetramethoxysilane, with K$_2$CrO$_4$, as follows. TlNO$_3$ (0.5 g) was dissolved in H$_2$O (20 ml) at room temperature. After 1 h, H$_2$O (27.5 ml) was added together with tetramethoxysilane (2.5 ml). The mixture was stirred for 70 min and then distributed into seven test tubes. The mixtures were left for 2 d until a firm gel formed. A solution of K$_2$CrO$_4$ (0.185 g) in H$_2$O (25 ml) was then prepared, i.e. in the approximate overall molar ratio of 2:1 for TlNO$_3$ and K$_2$CrO$_4$. A small quantity (about 3 ml) of this solution was introduced into each test tube in which the title crystals were to be grown. During the growth of the crystals, Liesegang rings developed: on the front of the precipitation zone the gel was yellow, while behind it had an orange tint. Crystals of two shapes and colours could be distinguished, namely one type that formed tiny cubes with a more intense orange colour and the other forming needle or plate-like crystals that were pale yellow. However, the diffraction patterns of either sample were the same. After four months, crystals were selected manually from the gel. Calorimetric measurements indicated the possible presence of the β-K$_2$SO$_4$ polymorph.

Differential scanning calorimetry experiments were performed using a Perkin–Elmer DSC 7 instrument for the measurements from 93 to 323 K and a Perkin–Elmer Pyris Diamond instrument for the measurements from 298 to 823 K (scanning rate 10 K min^{-1}, sample mass 17 mg, Al pans 40 µl). PYRIS software (Perkin–Elmer, 2001) was used for control and evaluation. A reversible phase transition was found at 783 K on heating and at 777 K on cooling (enthalpy change 4.0 J g^{-1}). This is in good agreement with the phase transitions observed for the β-K$_2$SO$_4$ polymorph of Tl$_2$CrO$_4$ by differential thermal analysis at 795 K on heating and 774 K on cooling (Natarajan & Secco, 1974).

Crystal data

Tl$_2$CrO$_4$	V = 999.06 (12) Å^3
M_r = 524.8	Z = 8
Monoclinic, $C2/m$	Mo $K\alpha$ radiation
a = 12.7458 (8) Å	μ = 66.39 mm^{-1}
b = 5.8070 (3) Å	T = 292 K
c = 14.721 (1) Å	$0.25 \times 0.03 \times 0.03$ mm
β = 113.519 (7)°	

inorganic compounds

Table 1
Bond-valence sums (Brese & O'Keeffe, 1991) and chemical strain GII (Brown, 2005) for the ions in the title structure and for some related structures.

The BVS were calculated for coordination up to 4Å. $A1$, $A2$ and B are the 11- and nine-coordinated cations and the anion, respectively.

	$Tl_2CrO_4{}^a$	$Tl_2CrO_4{}^b$	$Tl_2SeO_4{}^c$	$Tl_2SeO_4{}^d$
Tl1/$A1$	1.026 (8)	0.90 (6)	0.813 (13)	0.992 (17)
Tl2/$A2$	1.221 (13)	1.31 (8)	0.971 (14)	1.151 (18)
Tl3	1.150 (12)			
Tl4	1.070 (9)			
Cr1a/$B1$	5.67 (8)	5.5 (5)	6.34 (13)	5.77 (13)
O1a/O1	1.76 (6)	1.9 (3)	2.02 (7)	1.93 (6)
O2a/O2	2.03 (4)	1.9 (3)	2.03 (8)	2.03 (6)
O3a/O3	2.05 (3)	1.9 (2)	2.04 (6)	1.95 (7)
O4				2.00 (7)
Cr1b	5.65 (8)			
O1b	2.03 (6)			
O2b	1.79 (4)			
O3b	2.04 (3)			
GII	0.187 (19)	0.238 (155)	0.149 (52)	0.110 (40)

	$Tl_2SO_4{}^e$	$K_2SeO_4{}^f$	$K_2CrO_4{}^g$	$K_2SO_4{}^h$
$A1$	0.838 (6)	0.943 (7)	0.9358 (16)	1.0795 (18)
$A2$	0.990 (8)	1.273 (7)	1.301 (2)	1.324 (3)
B	6.09 (7)	6.24 (4)	5.966 (12)	5.997 (16)
O1	1.86 (4)	2.123 (15)	2.006 (7)	2.015 (10)
O2	2.07 (4)	2.12 (2)	2.076 (6)	2.152 (9)
O3	2.00 (3)	2.09 (3)	2.061 (6)	2.117 (7)
GII	0.092 (4)	0.161 (10)	0.125 (1)	0.152 (2)

References: (a) this work; (b) Carter & Margulis (1972); (c) 293 K: Friese *et al.* (2004); (d) 30 K: Friese *et al.* (2004); (e) Wallez *et al.* (2004); (f) González-Silgo *et al.* (1996); (g) Toriumi & Saito (1978); (h) Ojima *et al.* (1995).

Data collection

Oxford Gemini diffractometer
Absorption correction: analytical [*CrysAlis Pro* (Oxford Diffraction, 2009), analytical numerical absorption correction using a multifaceted crystal model (Clark & Reid, 1995); it seemed that one part of the sample did not diffract well and therefore dimensions of 0.065 × 0.034 × 0.027 mm were used]
$T_{min} = 0.055$, $T_{max} = 0.210$
5287 measured reflections
1363 independent reflections
710 reflections with $I > 3\sigma(I)$
$R_{int} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.086$
$S = 0.94$
1363 reflections
55 parameters
$\Delta\rho_{max} = 2.43$ e Å^{-3}
$\Delta\rho_{min} = -2.71$ e Å^{-3}

Two refined models were used, one with all atoms independent (79 parameters refined and with slightly lower refinement indicators: $R_{obs} = 0.0324$, $wR_{obs} = 0.0777$, $R_{all} = 0.0804$, $wR_{all} = 0.0841$, $S_{obs} = 1.22$ and $S_{all} = 0.93$; otherwise, the refinement conditions were the same), and the other where the atomic parameters were constrained in such a way that the independent chromates in the two positions were assumed to be identical, *i.e.* the atomic parameters of the reference chromate situated on the mirror plane were refined. Further refined parameters of the chromate were the rotation and the displacement parameters of the molecules in each site, in order to localize their true positions. Some rotations, however, were excluded, in order to respect the localization of the chromates on the crystallographic mirror planes, *i.e.* only the rotation whose axis is parallel to the y axis was released. (The rotation of the a chromate about the axis parallel

Table 2
Characteristics of Tl^+–Tl^+ pairs in the title structure.

$Tl^+\cdots Tl^+$ is the distance between the two cations of a pair; the symmetry code is given for the second cation. The Tl^+–O^{2-} column gives the minimum and maximum Tl^+–O^{2-} distances for the O atoms shared by the two cations. N is the number of shared O atoms in the coordination environment around the pairs of Tl^+ cations.

Pair	$Tl^+\cdots Tl^+$ (Å)	Tl^+–O^{2-} (Å)	N
Tl1/Tl1($-x + 2, y, -z + 1$)	3.7991 (14)	3.003 (15)–3.402 (12)	2
Tl1/Tl2(x, y, z)	3.9772 (15)	2.715 (9)–2.841 (7)	2
Tl1/Tl2($x + \frac{1}{2}, y - \frac{1}{2}, z$)	3.7733 (9)	2.826 (8)–3.402 (12)	3
Tl1/Tl2($x + \frac{1}{2}, y + \frac{1}{2}, z$)	3.7733 (9)	2.826 (8)–3.402 (12)	3
Tl1/Tl3($x + \frac{1}{2}, y + \frac{1}{2}, z$)	3.6053 (14)	2.826 (8)–3.047 (9)	4
Tl1/Tl4($x + \frac{1}{2}, y + \frac{1}{2}, z$)	4.4116 (17)	2.730 (9)–2.730 (9)	2
Tl3/Tl4(x, y, z)	4.0127 (14)	2.730 (9)–3.283 (15)	3
Tl3/Tl4($x - \frac{1}{2}, y - \frac{1}{2}, z$)	3.7513 (10)	2.854 (7)–3.286 (14)	3
Tl3/Tl4($x - \frac{1}{2}, y + \frac{1}{2}, z$)	3.7513 (10)	2.854 (7)–3.286 (14)	3
Tl4/Tl4($-x + 1, y, -z$)	3.7764 (17)	3.163 (10)–3.286 (14)	2

Table 3
Characteristics of Tl^+–Tl^+ pairs in the β-K_2SO_4 polymorph of Tl_2CrO_4 (Carter & Margulis, 1972).

Definitions are the same as in Table 2.

Pair	$Tl^+\cdots Tl^+$ (Å)	Tl^+–O^{2-} (Å)	N
Tl1/Tl1($x - \frac{1}{2}, -y, -z + 1$)	4.406 (7)	2.975 (10)–3.52 (8)	3
Tl1/Tl1($x + \frac{1}{2}, -y, -z + 1$)	4.406 (7)	2.975 (10)–3.52 (8)	3
Tl1/Tl2($-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$)	4.313 (8)	2.80 (5) –3.52 (8)	3
Tl1/Tl2($x, y - 1, z$)	3.992 (8)	2.70 (9) –3.08 (6)	3
Tl1/Tl2($x - \frac{1}{2}, -y + 1, -z$)	4.189 (7)	2.70 (9) –3.31 (5)	3
Tl1/Tl2($x + \frac{1}{2}, -y + 1, -z$)	4.189 (7)	2.70 (9) –3.31 (5)	3
Tl1/Tl2($-x, y - \frac{1}{2}, -z + \frac{1}{2}$)	3.938 (6)	2.80 (5) –3.80 (7)	4
Tl1/Tl2($-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$)	3.938 (6)	2.80 (5) –3.80 (7)	4
Tl2/Tl2($-x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$)	4.071 (9)	2.71 (8) –2.85 (8)	3
Tl2/Tl2($-x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$)	4.071 (9)	2.71 (8) –2.85 (8)	3

to y was excluded for computational reasons.) Also, the possible translations were limited because of the presence of the mirror plane. (For further details, see the refinement instruction file in the archived CIF.) The latter model, with the assumed identical independent chromates, was given preference, because the displacement parameters of some O atoms seemed to be more probable and the lowering of the refinement indicators was negligible with respect to the decrease of 24 in the number of refined parameters. The maximum residual electron-density peak (2.43 e Å^{-3}) is situated 0.2872 (11) Å from Tl3 at (x, y, z), while the minimum electron-density peak (-2.71 e Å^{-3}) is situated 1.2728 (12) Å from Tl2 at ($x - \frac{1}{2}, y - \frac{1}{2}, z$).

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *JANA2006*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3055). Services for accessing these data are described at the back of the journal.

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