

The Crystal Structure of α -Thallium Hexaiodochromate, α -Tl₄CrI₆

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Abstract

The preparation and crystal structure determination of α -Tl₄CrI₆ at 293 K, using a four-circle diffractometer, is reported. α -Tl₄CrI₆ is tetragonal, $P4/mnc$, $a = 9.131(1)$, $c = 9.668(1)$ Å, $Z = 2$. Least-squares refinement, using the weighting scheme $w_F = 1/\sigma_F^2$, resulted in $R_{wF} = 0.0142$ and $R_F = 0.0194$. α -Tl₄CrI₆ contains isolated CrI₆ octahedra with Tl⁺ ions in eight coordination in the form of a bicapped trigonal prism. Because of the Jahn–Teller effect the CrI₆ octahedra are elongated. No long-range order is found to occur at 293 K. Between 77 and 4.2 K α -Tl₄CrI₆ undergoes a phase transition to β -Tl₄CrI₆, which contains a long-range order of elongated octahedra. Unit-cell dimensions of isostructural iodides are reported.

Introduction

The structure determination of the title compound is part of an investigation of the compounds in the series $AI-BI_2$, A representing an alkali metal, In or Tl and B a first-row transition element, Mg, Zn, Cd or Hg. Several compounds A_4BI_6 could be prepared, all with axes comparable to those of Tl₄HgBr₆ (Broderson, Thiele & Goerz, 1973). These compounds, listed in Table 1, are most probably isostructural as their X-ray powder diffraction patterns show a strong resemblance. We were particularly interested in the Cr²⁺ compounds because they can show distortion due to the Jahn–Teller effect. DTA measurements exhibit a broad peak at about 162 K. Measurements on the single-crystal diffractometer did not reveal a change in the cell parameters at this temperature. Furthermore the neutron powder diffraction recordings at 300 and 77 K are similar. Between 77 and 4.2 K a phase transition occurs since neutron powder diffraction experiments at 77 and 4.2 K resulted in different diffraction patterns. The results of these diffraction experiments will be published elsewhere.

Neutron powder diffraction experiments on CsCrI₃ (Zandbergen & IJdo, 1980) and X-ray single-crystal diffraction measurements (Crama & Zandbergen, 1979) on CsCrI₃ and CsCrCl₃ give strong evidence for

Table 1. Compounds A_4BI_6 which are isostructural with α -Tl₄CrI₆

The unit-cell dimensions (except for α -Tl₄CrI₆) were determined at room temperature by least-squares refinement of 2θ values of Cu $K\alpha$ powder diffraction recordings.

| Compound | a (Å) | c (Å) | V (Å ³) | c/a |
|---------------------------------------|-----------|-----------|-----------------------|-------|
| In ₄ MgI ₆ | 8.967 (3) | 9.868 (5) | 793.4 (9) | 1.101 |
| Tl ₄ MgI ₆ | 9.112 (2) | 9.797 (2) | 813.4 (5) | 1.075 |
| In ₄ TlI ₆ | 8.954 (2) | 9.935 (3) | 796.7 (4) | 1.110 |
| Tl ₄ TlI ₆ | 9.056 (3) | 9.898 (6) | 811.6 (6) | 1.093 |
| In ₄ CrI ₆ | 9.008 (1) | 9.723 (3) | 789.0 (5) | 1.079 |
| Tl ₄ CrI ₆ | 9.131 (1) | 9.668 (1) | 806.1 (6) | 1.059 |
| In ₄ MnI ₆ | 8.981 (2) | 9.868 (7) | 785.9 (9) | 1.099 |
| Tl ₄ MnI ₆ | 9.093 (1) | 9.747 (4) | 805.9 (6) | 1.072 |
| Tl ₄ MnI ₆ (i) | 9.114 | 9.767 | 811.3 | 1.072 |
| Tl ₄ FeI ₆ | 9.103 (4) | 9.763 (6) | 809.0 (9) | 1.073 |
| In ₄ CdI ₆ | 9.054 (1) | 9.747 (2) | 799.0 (4) | 1.077 |
| Tl ₄ CdI ₆ | 9.225 (1) | 9.605 (2) | 817.4 (2) | 1.041 |
| Tl ₄ HgI ₆ | 9.423 (2) | 9.234 (3) | 820.0 (7) | 0.980 |
| Tl ₄ HgI ₆ (ii) | 9.529 (5) | 9.387 (7) | 852.4 (15) | 0.985 |

References: (i) Seifert & Kischka (1978). (ii) Broderson, Thiele & Goerz (1973).

the presence of elongated octahedra, both above and below the phase transition, due to the Jahn–Teller effect. Other experiments confirm this assumption [absorption spectra on CsCrCl₃ and RbCrCl₃ (Alcock, Putnick & Holt, 1976) and RbCrCl₃, CsCrCl₃ and Rb₂CrCl₄ (Koehler, 1976); EPR on CsCuCl₃ (Hirotsu, 1977)].

Apart from establishing the occurrence of distorted octahedra we also examined the structure of α -Tl₄CrI₆ because the coordination of the Tl⁺ ion can give information about the position of the lone pair of Tl⁺.

The compounds listed in Table 1 were prepared by melting a stoichiometric mixture of the binary compounds, and annealing – after powdering – for several weeks at temperatures just below the melting point. The binary compounds were purified by sublimation (BI_2) or distillation (InI and TlI). Single crystals of Tl₄CrI₆ were grown by the Bridgman method. As the compound is very hygroscopic, some P₂O₅ was placed in the capillary with the single crystal of Tl₄CrI₆. All manipulations were carried out in a dry glove box.

Table 2. *Single-crystal data of α -Ti₄CrI₆*

| | | | |
|--|--|-------------------------------|---|
| <i>a</i> | 9.131 (1) Å | $\mu(\text{Mo } K\alpha)$ | 52.49 mm ⁻¹ |
| <i>c</i> | 9.668 (1) | $\lambda(\text{Mo } K\alpha)$ | 0.71069 Å |
| <i>V</i> | 806.1 (6) Å ³ | Bragg angle | 2–30° |
| <i>Z</i> | 2 | Scan type | $\omega + 2\theta/3^*$ |
| Space group | <i>P4/mnc</i> | Scan angle | (1.1 + 0.9 tan θ)° in ω |
| <i>D_c</i> | 6.744(1) Mg m ⁻³ | Monochromator | Graphite |
| Reflexions used for absorption correction | 2̄1̄2̄ and 3̄3̄4̄ | | |
| Dimensions of the single crystal | 0.2 × 0.02 × 0.03 mm | | |
| Minimum and maximum transmission | 0.22, 0.49 | | |
| Systematically absent reflexions | <i>h</i> 0 <i>l</i> , <i>h</i> + <i>l</i> = 2 <i>n</i> + 1 <i>h</i> <i>h</i> <i>l</i> , <i>l</i> = 2 <i>n</i> + 1 | | |
| Measured reflexions | 2486 | | |
| Independent reflexions | | | |
| Significant | 643 | | |
| Non-significant† | 711 | | |
| Independent reflexions with <i>hkl</i> and <i>hkl</i> averaged | | | |
| Significant | 340 | | |
| Non-significant | 337 | | |

* During rotation of the crystal over x° , the detector is rotated over $2x/3^\circ$.

† Reflexions were regarded as non-significant when their intensity was less than 2σ .

The systematically absent reflexions for α -Ti₄CrI₆ (see Table 2) determined from zero- and upper-level Weissenberg photographs suggested the space groups *P4nc* and *P4/mnc*.

A single crystal was mounted on an Enraf–Nonius four-circle diffractometer. All reflexions were scanned at a speed of 20/3° min⁻¹; if the intensity was higher than 2σ , a final scan was made to achieve an accuracy of 1%, with a minimum speed of 0.5° min⁻¹. Crystallographic and technical data are given in Table 2. The cell parameters were determined by a least-squares procedure based on the optimized θ , ψ , χ and κ angles of 24 reflexions. The relatively high number of non-significant reflexions is caused by the non-significance of most reflexions in the Bragg-angle region of 25 to 30° and the special positions of most of the atoms giving rise to a large number of weak reflexions. In order to establish whether the space group is *P4nc* or *P4/mnc*, after each reflexion *hkl* the reflexion *hkl* was measured immediately.

After correction for absorption (de Graaff, 1973), and for Lorentz and polarization effects, the intensities were reduced to F_o values and symmetry-related reflexions were averaged. Scattering factors, taken from *International Tables for X-ray Crystallography* (1974), were used with the correction for the real and imaginary parts of the anomalous dispersion. The function minimized during the least-squares refinement was $\sum w_F(F_o - F_c)^2$, with the weighting scheme $w_F = 1/\sigma_F^2$, where σ is the estimated standard deviation due to counting statistics and errors in the absorption correction. For all calculations a set of computer programs by

R. A. G. de Graaff and E. W. M. Rutten-Keulemans was used.

The refinement was started with, as starting parameters, the positions of the ions in Ti₄HgBr₆. Full-matrix refinement in space group *P4nc* for *hkl* and *hkl* with a correction for extinction led to convergence at $R_{wF} = 0.0190$ and $R_F = 0.0232$. A similar refinement in space group *P4/mnc* converged at $R_{wF} = 0.0191$ and $R_F = 0.0234$.

It was concluded that the space group of α -Ti₄CrI₆ is *P4/mnc* because the lowering of the symmetry of the structure did not lead to significant shifts in the positional parameters (all less than half the standard deviation) and because the R values are not significantly lowered according to the R_F ratio test.

After the intensities *hkl* and *hkl* were averaged, the R values dropped to $R_{wF} = 0.0152$ and $R_F = 0.0206$ on refinement in space group *P4/mnc*.

The anisotropic thermal parameter in the *a* direction (U_{11}) of I(2) was found to be twice as large as those in the other directions (see Table 4). Because this is not found for the Br⁻ ion in Ti₄HgBr₆, and because elongated octahedra were expected, we divided the I(2)⁻ ion into two parts, thus creating a random distribution or short-range order of elongated octahedra (see also *Discussion*). With this alteration the R values dropped to $R_{wF} = 0.0142$ and $R_F = 0.0194$. According to the R_F ratio test the significance level of this model is larger than 99%. The shifts from the position of the undivided I(2)⁻ ion are much larger than the standard deviation. The thermal motion of the I(2)⁻ ion is fairly isotropic for the model with the divided I(2)⁻ ion. For these reasons we conclude that the model with a division of the I(2)⁻ ion gives a more adequate description of the structure of α -Ti₄CrI₆ than the model with a non-divided I(2)⁻ ion.

Positional and anisotropic thermal parameters are shown in Tables 3 and 4 respectively.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34692 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional parameters of α -Ti₄CrI₆*

I(2*a*) and I(2*b*) represent the positions of the divided I(2)⁻ ion. These positions are half occupied.

| | <i>x</i> | <i>y</i> | <i>z</i> |
|----------------|--------------|--------------|-------------|
| Ti | 0.14476 (3) | 0.35524 (3) | 0.25 |
| Cr | 0.0 | 0.0 | 0.0 |
| I(1) | 0.0 | 0.0 | 0.28330 (7) |
| I(2) | 0.30310 (8) | 0.14536 (8) | 0.0 |
| I(2 <i>a</i>) | 0.32127 (11) | 0.14536 (13) | 0.0 |
| I(2 <i>b</i>) | 0.28488 (14) | 0.13200 (14) | 0.0 |

Discussion

α - Tl_4CrI_6 contains isolated CrI_6 octahedra with Tl^+ ions in eight coordination in the form of a bicapped trigonal prism. A (001) projection of the structure is shown in Fig. 1. Some relevant distances and bond angles are listed in Table 5 and a projection of the TlI_8 polyhedron on the (001) plane is shown in Fig. 2. The Tl coordination in Tl_4CrI_6 is very similar to that in TlCdI_3 , viz. a three-capped trigonal prism with one I^- ion at larger distance (NH_4CdCl_3 structure, Zandbergen, Verschoor & IJdo, 1979). It is remarkable that although Rb^+ has almost the same radius as Tl^+ , and K^+ as In^+ , no K_4BI_6 , Rb_4BI_6 or Cs_4BI_6 compounds could be prepared. This may be due to the presence of lone pairs in Tl^+ and In^+ . The same occurs with the compounds TlMnI_3 and TlFeI_3 , which adopt the NH_4CdCl_3 structure, whereas no corresponding KBI_3 , RbBI_3 or CsBI_3 compounds exist with this structure. As can be seen in Fig. 2 the most obvious place for the lone pair of Tl^+ in α - Tl_4CrI_6 is along the twofold axis towards the other Tl^+ ion on that twofold axis. So the space between these two Tl^+ ions is occupied commonly by their lone pairs. The distance between these two Tl^+ ions is short, 3.74 Å, compared to the shortest

$\text{Tl}-\text{Tl}$ distance in TlI of 3.84 Å and taking into account that the two lone pairs are probably situated between these Tl^+ ions.

Although the In^+ ion is smaller than the Tl^+ ion the c axes of the In_4BI_6 compounds are larger than the c axes of the corresponding Tl_4BI_6 compounds. With the BI_6 octahedron assumed to be the same in both In_4BI_6 and Tl_4BI_6 , the introduction of a smaller cation will cause the BI_6 octahedra to move towards each other, resulting in a shorter a axis. As shown in Fig. 3 this contraction results in a shorter distance between the $\text{I}(2)^-$ ion of one octahedron and the $\text{I}(1)^-$ ion of an adjacent octahedron. The $\text{I}(1)^-$ ion will shift away from the approaching $\text{I}(2)^-$ ion. So the substitution of In^+ for Tl^+ should result in a longer c axis and a shorter a axis.

Table 4. Anisotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) of α - Tl_4CrI_6

| | U_{11} | U_{22} | U_{33} | $2U_{12}$ | $2U_{23}$ | $2U_{13}$ |
|---------|----------|----------|----------|-----------|-----------|-----------|
| Tl | 410 (1) | 410 (1) | 462 (2) | 53 (5) | -223 (3) | -223 (3) |
| Cr | 278 (11) | 278 (11) | 162 (12) | 0 | 0 | 0 |
| I(1) | 293 (3) | 293 (3) | 197 (3) | 0 | 0 | 0 |
| I(2) | 612 (5) | 297 (4) | 252 (3) | 220 (8) | 0 | 0 |
| I(2a,b) | 292 (3) | 260 (3) | 254 (3) | -14 (8) | 0 | 0 |

Table 5. Some relevant distances (Å) and bond angles ($^\circ$)

For Cr-I distances, values are given for the undivided and the divided $\text{I}(2)$ ion. The subscript on the I^- ion refers to the numbering of the I^- ions in Fig. 2.

| | | | |
|---|--------------|---|--------------|
| Cr-I(1) | 2.739 (1) 2x | Tl-I(1) | 3.517 (1) 2x |
| Cr-I(2) | 3.044 (1) 4x | Tl-I(2) | 3.441 (1) 2x |
| Cr-I(2a) | 3.220 (1) 2x | Tl-I(2) | 3.573 (1) 2x |
| Cr-I(2b) | 2.867 (1) 2x | Tl-I(2) | 3.947 (1) 2x |
| I(1)-I(1) | 4.190 (1) | I(2) ₂ -I(2) ₄ | 4.304 (1) |
| I(1) ₃ -I(2) ₂ | 4.094 (1) | I(2) ₂ -I(2) ₈ | 4.398 (2) |
| I(1) ₃ -I(2) ₁ | 4.302 (1) | | |
| I(2a)-Cr-I(2b) | 89.48 (4) | I(2) ₂ -Tl-I(1) ₃ | 70.54 (2) |
| I(2) ₁ -Tl-I(2) ₂ | 81.00 (2) | I(2) ₂ -Tl-I(2) ₄ | 75.68 (3) |
| I(2) ₁ -Tl-I(1) ₃ | 70.11 (2) | I(2) ₂ -Tl-I(2) ₅ | 146.65 (1) |
| I(2) ₁ -Tl-I(2) ₄ | 140.38 (2) | I(2) ₂ -Tl-I(1) ₆ | 131.01 (2) |
| I(2) ₁ -Tl-I(2) ₅ | 91.71 (3) | I(1) ₃ -Tl-I(2) ₄ | 72.08 (2) |
| I(2) ₁ -Tl-I(1) ₆ | 141.23 (2) | I(1) ₃ -Tl-I(2) ₅ | 76.36 (2) |
| I(2) ₁ -Tl-I(2) ₇ | 71.39 (3) | I(1) ₃ -Tl-I(1) ₆ | 134.54 (1) |
| I(2) ₁ -Tl-I(2) ₈ | 130.58 (4) | I(2) ₄ -Tl-I(2) ₅ | 90.60 (3) |

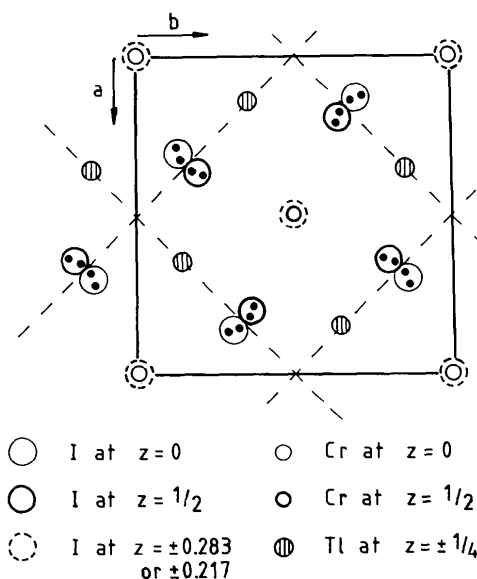


Fig. 1. A projection of the structure of α - Tl_4CrI_6 on the (001) plane. The positions of the divided $\text{I}(2)$ ion are indicated by filled circles.

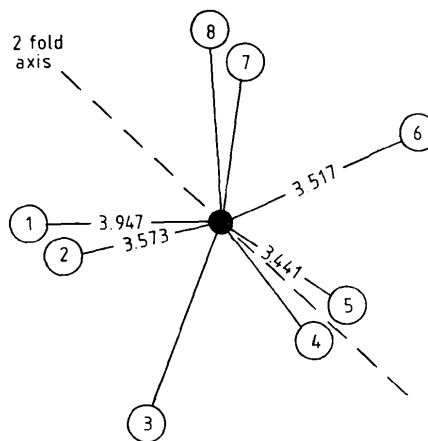


Fig. 2. A projection on the (001) plane of the TlI_8 polyhedron. The numbers refer to the subscripts on the I^- ions in Table 5.

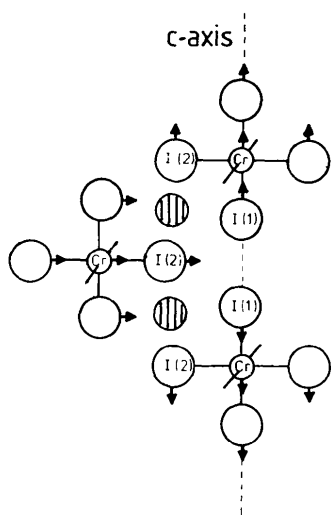


Fig. 3. The effect of the substitution of In^+ for Tl^+ (indicated by hatched circles) in Tl_4BI_6 compounds. It causes the BI_6 octahedra to move towards each other, resulting in a longer c axis.

The different c/a ratio of the compound Tl_4HgI_6 is caused by the occurrence of HgI_2 molecules, as is discussed by Broderon, Thiele & Goerz (1973).

Another interesting aspect of $\alpha\text{-Tl}_4\text{CrI}_6$ is the existence of Jahn–Teller distorted octahedra in this compound. The c axis of $\alpha\text{-Tl}_4\text{CrI}_6$ is smaller than those of comparable Tl_4BI_6 compounds (see Table 1). This shortening of the c axis can be obtained by introduction of octahedra, shortened in the [001] direction or elongated in the (001) plane. Clearly, a shortening can easily be realized in the structure as the two Cr–I distances in the [001] direction are 2.72 Å compared to the four averaged Cr–I distances in the (001) plane of 3.04 Å. An elongation can be obtained by a shift of the $\text{I}(2)^-$ ions in the (001) mirror plane. Introduction of octahedra with their elongation direction perpendicular to the c axis leads to the destruction of the fourfold axis along the c axis. Therefore, no long-range order of elongated octahedra is possible, as the unit cell found for $\alpha\text{-Tl}_4\text{CrI}_6$ is tetragonal. This leaves, as possibilities

besides octahedra shortened in the [001] direction, a short-range order or random distribution of octahedra, elongated in the (001) plane. The latter two possibilities, which cannot be distinguished by means of X-ray diffraction, can be accounted for by dividing each $\text{I}(2)^-$ ion into two parts. This model was refined, giving with respect to the model with the undivided $\text{I}(2)^-$ ion R values significantly lower and shifts of the divided $\text{I}(2)^-$ ions much larger than the standard deviation. It is concluded that in $\alpha\text{-Tl}_4\text{CrI}_6$ the CrI_6 octahedra are elongated. This conclusion is in accordance with the neutron powder diffraction experiments at 4.2 K which suggest that the unit cell becomes orthorhombic with axes of about $a\sqrt{2}$, $a\sqrt{2}$, c . At this temperature there exists a long-range order of elongated octahedra as can be seen from the absence of the fourfold axis.

Although the structure favours a shortening of the octahedra, an elongation is still found to occur, which apparently is more favourable than a shortening.

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