

## The Crystal Structure of the 1:4 Thallous Chlorate–Thiourea Complex

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(Received 5 August 1969)

The three-dimensional structure of  $\text{TlClO}_3 \cdot 4(\text{SCN}_2\text{H}_4)$  has been determined by means of data collected with an X-ray single-crystal diffractometer. After full-matrix least-squares refinement a discrepancy of 5.5% between observed and calculated structure factors for 1519 measured intensities was observed. The cations and anions were found to be completely segregated. The thallous ions occur along [001] in a linear chain which is surrounded by sulphur atoms arranged anti-prismatically around individual thallous ions. The amine ends of the thiourea molecules enclose the chlorate ions in elliptical channels parallel to [001]. The chlorine atom and the three oxygen atoms composing the chlorate ion lie at the apices of a distorted tetrahedron and no indications of hydrogen bonding have been observed.

### Introduction

The ionic salt complexes of thiourea, with the  $\text{TlClO}_3$  complex as the only exception, are characterized by fairly high symmetry (Boeyens & Herbstein, 1967). The geometry of the chlorate ion is undoubtedly responsible for the anomalous behaviour and the mechanism whereby it lowers the symmetry of the complex can only be determined through a structural study.

### Experimental

Crystals of the complex were obtained from an aqueous solution of its components. The crystals are monoclinic and the unit-cell dimensions as refined on a four-circle Hilger & Watts diffractometer are:  $a = 22.037 \pm 0.011$ ,  $b = 9.869 \pm 0.005$ ,  $c = 8.201 \pm 0.004$  Å,  $\gamma = 103.95 \pm 0.01^\circ$ . The density calculated for four formula units per unit cell is  $2.21 \text{ g.cm}^{-3}$  compared with the measured density (Boeyens & Herbstein, 1967) of  $2.20 \text{ g.cm}^{-3}$ . The condition limiting possible reflexions is:  $hkl$  for  $h+l=2n$ . The structure was solved successfully assuming the centrosymmetric space group  $B2/m$  which is consistent with the reflexion condition.

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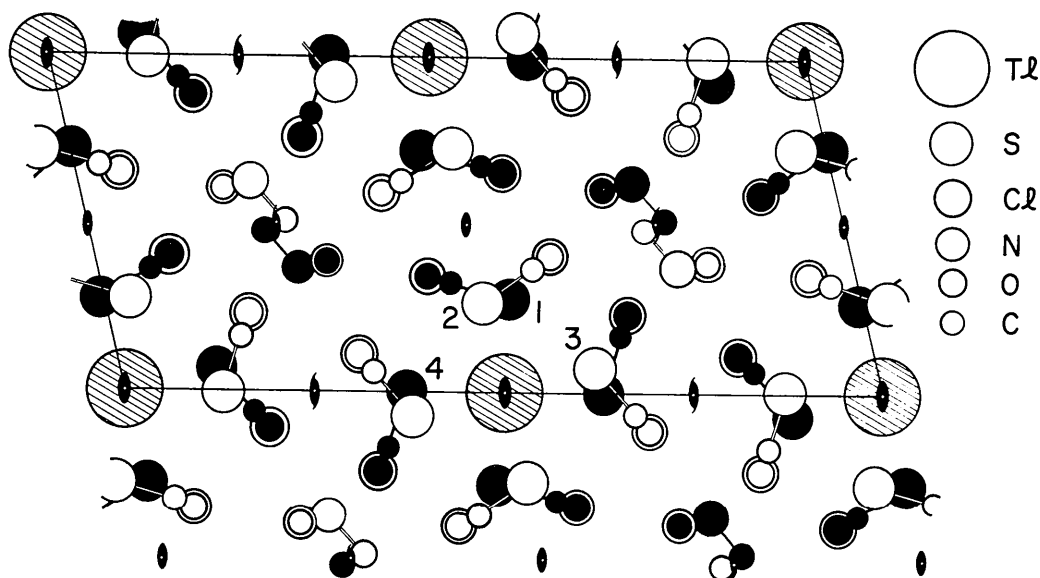


Fig. 1. Projection of the structure along [001]. Atoms represented by open and solid circles belong to molecules lying across the mirror planes at  $z=0$  and  $\frac{1}{2}$  respectively. Concentric circles represent mirrored pairs of either nitrogen or oxygen atoms which overlap in projection. Striped circles represent Tl atoms at  $z \approx \frac{1}{4}$  and  $\frac{3}{4}$ .

A needle-shaped crystal ( $0.042 \times 0.084$  mm) was used to collect 2784 intensities (the complete copper sphere) using Mo  $K\alpha$  (Zr filter) radiation and an  $\omega$ -scan on the Hilger & Watts instrument. All the usual corrections as described recently (Roux & Boeyens, 1970) were applied and only the 1519 reflexions with intensities above significance level were given non-zero uniform weight in the final refinement (Dunning & Vand, 1969). All computer programs and scattering factor tables used in the analysis had been described before (Roux & Boeyens, 1969).

### Determination and refinement of the structure

A three-dimensional Patterson synthesis was calculated on an IBM 360/65 computer. The Tl-Tl vectors were readily identified and from the other peaks in evidence the positions of Cl and S relative to Tl could be established. All available evidence indicated the thiourea molecules and chlorate ions to lie across the mirror planes at  $z=0, \frac{1}{2}$  so that Tl atoms could be placed in any of the (e) or (g) fourfold positions, or their equivalent sets. The notation used here is that of *International Tables for X-ray Crystallography* (1965) for space group no. 12. Positions (g) which are of the type 00z are only allowed for  $z \approx \frac{1}{2}$ . Inspection revealed that occupation of positions (e) would entail unrealistically short interatomic distances between neighbouring chlorate groups.

A Fourier synthesis with Tl in (g) gave a trial structure which could be refined directly. Full-matrix refinement of the atomic parameters and anisotropic temperature factors was considered complete when all parameter shifts were less than 0.1 of their estimated standard deviations. At termination the conventional  $R$  index was 0.055.

The final atomic and thermal parameters of the atoms in the asymmetric unit are listed in Table 1 and the observed and calculated structure factors on an absolute scale in Table 2;  $F(000) = 1064$ .

### Description of the structure

An excellent view of the structure is provided by the projection along [001], shown in Fig. 1.

The main feature of the structure is the occurrence of infinite coordination columns of composition  $\text{Tl}^+ \cdot 4$  thiourea which lie along [001]. The interthallium distances within the column are not constant, but alternate between the two values  $4.148 \pm 0.003$  and  $4.053 \pm 0.003$  Å. There are four independent Tl-S distances of

$$\left. \begin{array}{l} \text{Tl-S(1): } 3.330 \\ \text{Tl-S(2): } 3.386 \\ \text{Tl-S(3): } 3.431 \\ \text{Tl-S(4): } 3.509 \end{array} \right\} \pm 0.018 \text{ \AA}$$

The four sulphur atoms in the same mirror plane do thus not define a perfect square and this is also evident

Table 1. Fractional coordinates and anisotropic thermal parameters ( $\times 10^5$ )

$$T = \exp [-(h^2\beta_{11} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

Standard deviations are given in parentheses.

	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Tl	0	0	0.24708 (15)	257 (2)	799 (8)	1290 (12)	61 (3)	0	0
S(1)	0.03622 (26)	0.27555 (51)	0	158 (12)	776 (54)	949 (78)	116 (21)	0	0
S(2)	0.49604 (27)	0.26896 (55)	0	151 (13)	897 (59)	981 (81)	-4 (22)	0	0
S(3)	0.37220 (27)	0.92889 (54)	0	203 (14)	698 (53)	1033 (81)	74 (22)	0	0
S(4)	0.12949 (29)	0.99558 (54)	0	237 (15)	595 (50)	1058 (81)	-18 (23)	0	0
Cl	0.23123 (24)	0.62830 (48)	0	146 (11)	691 (49)	1207 (81)	-2 (19)	0	0
O(1)	0.26381 (72)	0.51649 (165)	0	210 (51)	939 (193)	2660 (379)	133 (80)	0	0
O(2)	0.19059 (60)	0.61098 (140)	0.14131 (165)	304 (36)	2217 (209)	1515 (228)	249 (71)	110 (79)	105 (188)
N(1)	0.06109 (57)	0.65697 (110)	0.13621 (154)	229 (31)	751 (115)	1059 (190)	87 (49)	-68 (68)	21 (130)
N(2)	0.39832 (56)	0.59203 (112)	0.13884 (158)	213 (31)	841 (125)	1139 (201)	64 (50)	67 (69)	148 (136)
N(3)	0.32137 (70)	0.11435 (141)	0.14120 (177)	321 (41)	1408 (176)	1228 (227)	280 (71)	16 (86)	-191 (173)
N(4)	0.18726 (60)	0.23377 (112)	0.13802 (162)	254 (34)	768 (122)	1193 (205)	20 (52)	-52 (73)	-221 (136)
C(1)	0.03373 (89)	0.67515 (159)	0	176 (46)	347 (152)	741 (263)	43 (69)	0	0
C(2)	0.42811 (97)	0.63193 (176)	0	204 (52)	408 (178)	1046 (319)	85 (79)	0	0
C(3)	0.33531 (97)	0.06137 (216)	0	152 (49)	1001 (246)	1221 (359)	111 (90)	0	0
C(4)	0.17051 (93)	0.16855 (204)	0	146 (47)	916 (229)	1155 (337)	133 (85)	0	0

Table 2. Observed and calculated structure factors on an absolute scale

Table with multiple columns containing numerical data for structure factors. The columns are organized into groups, likely representing different reflections or indices. The data includes observed values and calculated values for various h, k, l indices.

Table 3. *Dimensions of the thiourea group*

	S-C	C-N	N-N	N-C-N
1	1.72 Å	1.30 Å	2.23 Å	118°
2	1.72	1.33	2.28	118
3	1.70	1.34	2.32	120
4	1.73	1.31	2.26	119
$\sigma$	0.02	0.02	0.03	2.0
UC TU	1.746 ± 0.008	1.349 ± 0.003		116.7 ± 0.2
TU in CC	1.76 ± 0.02	1.30 ± 0.04		120.4 ± 2.6

from the different S-S-S angles of 94.6, 91.2, 88.8 and 85.4° at S(1), S(2), S(3) and S(4) respectively. These slight distortions are related to nearest-neighbour approaches between nitrogen and oxygen atoms:

$$\left. \begin{array}{l} \text{N(1)-O: } 2.996 \\ \text{N(2)-O: } 3.094 \\ \text{N(4)-O: } 3.105 \end{array} \right\} \pm 0.02 \text{ \AA}$$

Although no attempt was made to locate hydrogen atoms, these values all appear to be too long to represent hydrogen bonds (Verhoef & Boeyens, 1968).

The dimensions of the four independent thiourea molecules (TU) are summarized in Table 3 together with the dimensions for uncoordinated thiourea (UC) (Elcombe & Taylor, 1968) as well as for thiourea in a typical coordination complex (CC), *viz.* with cadmium formate (Nardelli, Gasparri & Boldrini, 1965).

The geometry of the chlorate ion is also as expected. The actual parameters are:

Cl-O	O-O	O-Cl-O
1.449 ± 0.015 Å	2.318 ± 0.027 Å	106.2 ± 1.1°
1.454 ± 0.018	2.354 ± 0.022	108.3 ± 0.8

giving average dimensions: Cl-O = 1.45 ± 0.02; O-O = 2.34 ± 0.025 Å; O-Cl-O = 107 ± 1; O-O-O = 60.0 ± 1°.

### Discussion of the structure

It was pointed out before (Verhoef & Boeyens, 1969) that in the absence of complicating factors such as hydrogen bonding, the structures of all ionic thiourea complexes can be described in terms of coordination columns with fourfold symmetry. Not only is the nature of the anion responsible for distortions in these coordination columns, but it also determines their mutual arrangement. They pack together in such a way as to optimally surround the associated anions with the partially positive amino ends of the thiourea molecules. Spherical (Kruger & Boeyens, 1968) or highly symmetrical (Boeyens & Herbstein, 1967) anions occur in

channels among tetragonally arranged coordination columns. Elongated anions such as hydrated fluoride (Boeyens, 1968a) require an orthorhombic packing of the columns.

A similar arrangement is encountered in the present structure, the only difference being the oblique cell geometry. In the hydrated complexes, including the chloride complexes (Boeyens, 1968b) the anions can formally be considered as linear rods which line up to form flat sheets parallel to [001] and which can be approached equally closely by amino groups from both sides so as to define an orthogonal channel. In the present circumstances, however, the angular anions cannot line up like this. The resulting sheet contains a 2<sub>1</sub> axis and oxygen atoms which protrude at the edges give a z shaped appearance to the sheet in projection along [001]. To enclose this arrangement of anions by close-packed amine groups an oblique channel and hence monoclinic symmetry are required.

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