DL-Cysteinatothallium(I)*

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Abstract. $TlSO_2NC_3H_6$, M_r = 324·5, monoclinic, $P2_1/a$, a = 10·841 (6), b = 7·672 (2), c = 8·391 (2) Å, β = 114·58 (3)°, U = 634·6 Å^3, Z = 4, D_x = 3·40 g cm^{-3}, μ(Mo $K\alpha$) = 260 cm^{-1}, $F(000)$ = 576. The complex forms centrosymmetric Tl_2(D-cysteinate)(L-cysteinate) dimers in which each Tl atom is bonded to the carboxyl and thiol groups of both ligands [Tl–O = 2·86 (1), 3·06 (1); Tl–S = 2·890 (3), 3·090 (4) Å]. The Tl coordination is approximately square-pyramidal with the lone-pair electrons occupying the apex. Adjacent dimers in the crystal are linked by weak Tl–S bonds and by hydrogen bonds of the types N–H···O and N–H···S.

Introduction. The present complex is one of several Tl^I complexes crystallized as part of a study of metal–cysteine and metal–penicillamine complexes. A mixture of two types of crystals was obtained when a solution containing DL-cysteine and TlNO$_3$ at pH 8 was heated on a steam bath. The major component of the mixture consisted of thin yellow plates which were unsuitable for diffraction experiments. The minor component consisted of colourless diamond-shaped crystals. The mixture (from which crystals of either type could be separated only by hand) had analytical figures corresponding to DL-cysteinatothallium(I), Tl(DL-CysH), where CysH = $^+NH_3$–CH(CH$_2$–S$^-$)–COO$^-$. [Calculated for TlC$_3$H$_6$NO$_2$S: C = 11·09, H = 1·85, N = 4·31, S = 9·86%. Found: C = 11·2, H = 2·03, N = 4·52, S = 10·0%.] Crystals of the minor component were used for the present work.

Data were recorded to a limit of 2θ = 85° [Mo $K\alpha$ radiation, graphite monochromator, λ(Mo $K\alpha$) = 0·71069 Å] on a computer-controlled Supper equi-inclination diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970) with the ω-scan technique. Complete data sets were recorded for two crystals mounted to rotate about their a and b axes respectively. Both crystals had well-developed faces of the forms (22$\bar{1}$) and (001). One specimen had perpendicular distances of 0·164 and 0·160 mm between two pairs of parallel faces of the first form, and a distance of 0·110 mm between the two faces of the second form. In the second specimen the corresponding distances were 0·142, 0·128 and 0·080 mm respectively. Each

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reflexion was assigned an intensity $I = P - (B_1 + B_2)$ and variance $\sigma^2(I) = P + B_1 + B_2$, where P was the integrated peak count and the background counts B_1 and B_2 were measured during a total time equal to that required to measure P. Reflexions for which $I < 3\sigma(I)$ were considered to be unobservably weak. The data were corrected for Lorentz and polarization effects but not for extinction. Absorption corrections were applied by the Gaussian integration method using a 6 × 6 × 6 grid (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1965). Trial calculations showed that the errors introduced by the use of a 6 × 6 × 6 grid instead of, say, a 12 × 12 × 12 grid were of the order of 3%, but that the absorption corrections were more sensitive to small errors in the crystal dimensions than to changes in the grid size. For instance, an error of only 0·005 mm in the dimension perpendicular to (001) was capable of causing the relative absorption corrections to change anisotropically by as much as 10%. The data were placed on a common scale by the method of Rae (1965) and Rae & Blake (1966). Standard deviations $\sigma(F)$ were calculated taking into account both random and estimated systematic errors (Freeman & Guss, 1972). The final data set consisted of 2917 independent data of which 1145 were considered to be unobservably weak. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where weights $w = \sigma^{-2}(F)$ were calculated as above. Unobservably weak reflexions were given zero weight. Scattering factors for Tl, S, O, N and C, and anomalous dispersion terms for Tl and S, were from *International Tables for X-ray Crystallography* (1974).

In the final cycle all atoms except C had anisotropic temperature factors, and no parameter changed by more than 0·1 of its estimated standard deviation. Inclusion of anisotropic thermal parameters for the C atoms did not produce a significant decrease in the residual R (Hamilton, 1965). Nine intense low-angle reflexions judged to be suffering from severe extinction and 28 low-angle reflexions on upper layers which were found on review to have been affected by instrumental errors were deleted from the data set. The final residual for the observed reflexions, $R = \sum ||F_o| - |F_c||/\sum |F_o|$, was 0·063, the weighted residual, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0·072, and the mean error in an

Table 1. Final fractional positional coordinates ($\times 10^4$) for DL-cysteinatothallium (I)

Here and in Table 2, a number in parentheses represents the standard deviation right-adjusted to the least significant digit of the preceding quantity.

	x	y	z
Tl	−383·7 (5)	2604·0 (6)	4384·7 (7)
S	2060 (3)	138 (4)	5211·(4)
O(1)	1006 (10)	2694 (14)	8126 (15)
O(2)	1069 (11)	−157 (16)	8751 (15)
N	3523 (10)	2850 (13)	8378 (12)
C(1)	3058 (12)	1119 (14)	8726 (14)
C(2)	1599 (14)	1225 (16)	8512 (16)
C(3)	3235 (14)	−227 (16)	7513 (16)

observation of unit weight was 1·400. The validity of the weighting scheme was shown by the lack of dependence of $\langle w|F_o - F_c|^2 \rangle$ on both F_o and sin θ. An $(F_o - F_c)$ synthesis showed two positive and five negative peaks near the Tl atom. These peaks had integrated electron densities corresponding to 1·5 to 2 e. We attribute them to inadequate corrections for absorption. No other peak had an integrated electron density greater than 1 e. The final atomic positional and thermal parameters are listed in Table 1.*

Discussion. A view of the complex and explanation of the atomic labels are given in Fig. 1. The principal bond lengths and angles are listed in Table 2. The complex is a dimer in which the Tl atom is bonded to two O and

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32676 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

two S atoms. There is evidence (see below) that an additional coordination position is effectively taken up by a lone pair of electrons (*i.e.* that the lone-pair electrons are 'stereochemically active'). The coordination geometry is irregular. It may be derived from either a square-pyramidal or a trigonal-bipyramidal configuration. If we start from a square-pyramidal configuration then the lone-pair electrons occupy the

Table 2. Interatomic distances and bond angles

Superscript

(i)	$-x$,	$-y$,	$1-z$
(ii)	$x - \frac{1}{2}$,	$\frac{1}{2} - y$,	z
(iii)	$x + \frac{1}{2}$,	$\frac{1}{2} - y$,	z
(iv)	$\frac{1}{2} - x$,	$y + \frac{1}{2}$,	$2 - z$
(v)	$\frac{1}{2} - x$,	$y + \frac{1}{2}$,	$1 - z$
(vi)	$\frac{1}{2} - x$,	$y - \frac{1}{2}$,	$1 - z$

Tl—O(1)	2·86 (1) Å	S—C(3)	1·84 (1) Å
Tl—O(2^i)	3·06 (1)	C(3)—C(1)	1·52 (2)
Tl—S^i	2·890 (3)	C(1)—N	1·49 (2)
Tl—S	3·090 (4)	C(1)—C(2)	1·52 (2)
Tl···S^{ii}	3·573 (4)	C(2)—O(1)	1·27 (2)
N···O(1^{iii})	2·82 (2)	C(2)—O(2)	1·26 (2)
N···O(2^{iv})	2·73 (2)		
N···S^v	3·31 (1)		

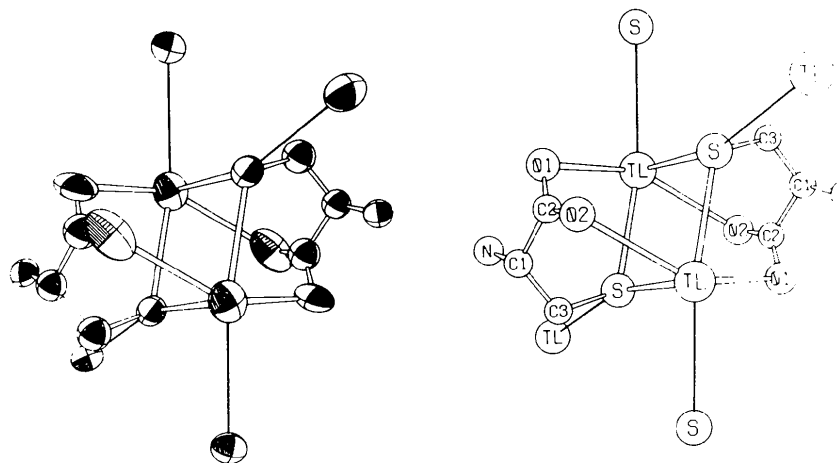|			
O(1)—Tl—O(2^i)	141·8 (3)°	S—C(3)—C(1)	112·0 (9)°
O(1)—Tl—S	76·0 (2)	C(3)—C(1)—N	109·1 (9)
O(1)—Tl—S^i	87·6 (2)	C(3)—C(1)—C(2)	112 (1)
O(2^i)—Tl—S	72·3 (2)	N—C(1)—C(2)	110·5 (9)
O(2^i)—Tl—S^i	73·4 (2)	C(1)—C(2)—O(1)	118 (1)
S—Tl—S^i	92·9 (1)	C(1)—C(2)—O(2)	117 (1)
C(3)—S—Tl	118·9 (4)	O(1)—C(2)—O(2)	125 (1)
C(3)—S—Tl^i	87·7 (4)	C(2)—O(1)—Tl	103·8 (8)
C(3)—S···N^{vi}	131·4 (5)	C(2)—O(2)—Tl^i	110·0 (8)
Tl—S—Tl^i	87·1 (1)		
Tl—S···N^{vi}	107·4 (2)		
Tl^i—S···N^{vi}	80·2 (2)		

Fig. 1. Thermal ellipsoids (50% probability) and atomic labels for Tl(DL-CysH). The long contacts between Tl and S atoms in different dimers are shown (thin bonds).
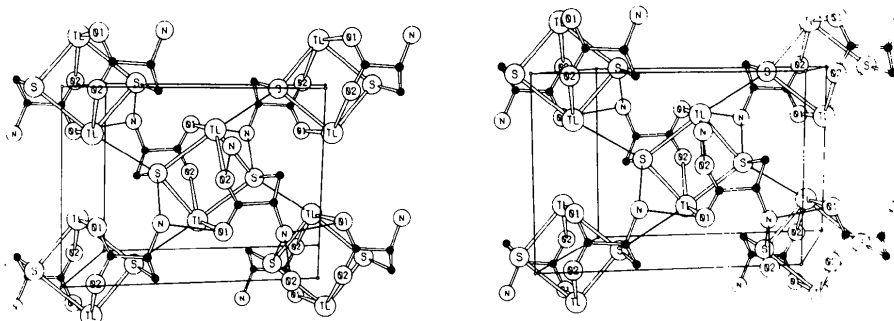
Fig. 2. Stereoview of crystal packing in Tl(DL-CysH). Thin bonds are hydrogen bonds or long Tl—S contacts. The origin is in the bottom left-hand corner distant from the observer. The x axis is horizontal (left to right), the y axis is vertical (bottom to top) and the z axis points towards the observer.

apex, and the two O and two S atoms occupy pairs of opposite corners of the base. The O—Tl—O angle is adjusted to 141° and the S—Tl—S angle to 93°, so that the two O atoms lie 'above' and the two S atoms 'below' a plane fitted to the four atoms. Alternatively we may start from a trigonal-bipyramidal arrangement with the two Tl—O bonds axial and the two Tl—S bonds and the lone pair equatorial. The S—Tl—S angle is then reduced to 93°, and the Tl—O bonds are bent away from the lone-pair direction until the O—Tl—O angle is 141°.

The nearest neighbour of the Tl atom on the side distant from the two O and two S ligand atoms is a S atom of an adjacent dimer [Tl···S = 3·573 (4) Å]. We regard this contact as non-bonding. The Tl atom has no other contacts shorter than 3·72 Å with atoms outside its own dimer. The fact that all the identifiable bonds lie on one side of the Tl atom indicates that the lone-pair electrons are stereochemically active.

The Tl—S bond lengths fall near the values found for Tl—S bonds in Tl^I dithiocarbamates, 2·97 to 3·29 Å. [For a summary of Tl^I dithiocarbamates see Elfwing, Anacker-Eickhoff, Jennische & Hesse (1976).]

The Tl—O bond lengths lie at the upper end of the range 2·6 to 3·0 Å found by Hughes (1973) for Tl^I ascorbate. Tl—O distances of 2·65 and 2·98 Å from a carboxyl group to a single Tl atom occur in salicylato-(1,10-phenanthroline)thallium(I) (Hughes & Truter, 1972). The ligand dimensions in Tl(DL-CysH) do not differ significantly from those of the free ligand, CysH$_2$ (Kerr, Ashmore & Koetzle, 1975). In the complex, the carboxyl and —NH$_3^+$ groups are coplanar, while in CysH$_2$ the carboxyl group is rotated from the C—C—N plane by 17° about the C—C bond. The conformation found here is also found in two of the three ligands in Sb(L-CysH)$_3$.H$_2$O where the Sb is bound only by three S atoms (Freeman & Moore, unpublished observations).

The dimers are notable for a planar four-membered ring containing two Tl and two S atoms, fused to an eight-membered ring composed of the same two Tl atoms and the two carboxyl groups. There are also

several six-membered rings involving Tl, O and S. There are no Tl—N bonds, in contrast to the Tl—N bonding in salicylato(1,10-phenanthroline)thallium(I) (Hughes & Truter, 1972).

There are three hydrogen bonds involving the —NH$_3^+$ group (Table 2 and Fig. 2). Two of these are strong bonds to carboxyl O atoms. The third is a weak bond to a S atom [C—N···S = 134°, N···S = 3·31 Å, sum of van der Waals radii = 3·4 Å (Hamilton & Ibers, 1968)]. The four bonds formed by the cysteine S atom (the hydrogen bond, the S—C$_\beta$ bond and two S—Tl bonds) have a distorted tetrahedral configuration.

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