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(DL-Tryptophanato)dimethylthallium(III) Monohydrate

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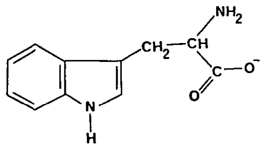
Abstract. $TlO_3N_2C_{13}H_{19}$, $M_r = 455{\cdot}3$, monoclinic, $P2_1/c$, $a = 7{\cdot}955$ (3), $b = 19{\cdot}507(2)$, $c = 10{\cdot}679$ (4) Å, $\beta = 117{\cdot}52$ (3)°, $U = 1471{\cdot}5$ Å^3, $Z = 4$, $D_c = 2{\cdot}05$ g cm^{-3}, μ(Mo $K\alpha$) = 105 cm^{-1}, $F(000) = 866$. The complex forms centrosymmetric $[(CH_3)_2Tl]_2$(D-tryptophan)(L-tryptophan) dimers in which each Tl atom is bonded to one O atom and one N atom of an amino acid residue with the carboxyl group acting as a monodentate bridging group [Tl—C = 2·11 (1), 2·12 (1); Tl—O = 2·47 (1), 2·59 (1); Tl—N = 2·66 (1) Å]. The coordination at the Tl atom is irregular and a vacant sixth coordination site is taken up by an essentially non-bonding contact (3·43 Å) from the pyrrole N atom of a parallel dimer set. Adjacent dimers in the crystal are held together in polymeric chains by hydrogen bonding between the molecule of water of crystallization and the pyrrole N—H.

Introduction. The title complex is one of several dimethylthallium(III) complexes prepared as part of a study of metal–amino acid bonding modes in solution and in the solid state. The crystals were obtained as colourless hexagonal prisms when a solution containing DL-tryptophan and $(CH_3)_2Tl(OAc)$ (Kurosawa & Okawara, 1967) at pH 7 was heated on a steam bath and then cooled to room temperature. The compound was analysed as (DL-tryptophanato)dimethylthallium(III) monohydrate, $(CH_3)_2Tl$(DL-TRP)$.H_2O$, where TRP stands for:



(Calculated for $TlC_{13}H_{19}N_2O_3$: C = 34·26, H = 4·17, N = 6·15%. Found: C = 34·4, H = 4·0, N = 6·4%.)

Data were recorded in the $3 \le \theta \le 30°$ range [Mo $K\alpha$ radiation, graphite monochromator, λ(Mo $K\alpha$) = 0·71069 Å] on a Philips PW1100 automatic four-circle diffractometer with a θ–2θ scan mode. Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not further examined (I_t is the intensity at the top of the reflection peak and I_b is the mean of two preliminary 5 s background measurements on either side). Of the remaining reflections, those for which the total intensity recorded in the first scan (I_i) was < 500 counts were scanned twice to increase their accuracy. A constant scan speed of 0·06° s^{-1} and a variable scan width of (0·65 + 0·1 tan θ)° were used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 5 h during data collection and showed no significant variations in intensity. The intensities were calculated from the peak and background measurements with a program written for the PW1100 diffractometer (Hornstra & Stubbe, 1972). The variance of intensity, I, was calculated as the sum of the variance due to counting statistics and $(0{\cdot}04I)^2$, where the term in I^2 was introduced to allow for other sources of error (Corfield, Doedens & Ibers, 1967). I and $\sigma(I)$ were corrected for Lorentz and polarization factors. No absorption corrections were

Table 1. *Fractional coordinates* (× 10^4) (*in the monoclinic space group* $P2_1/n$ *with* $c = 9{\cdot}952$ Å, $\beta = 107{\cdot}67°$) *and isotropic thermal parameters* (× 10^{-3} Å^2), *with e.s.d.'s in parentheses*

	x	*y*	*z*	*U*
Tl	165 (1)	661 (1)	3423 (1)	
C(1*m*)	779 (18)	−172 (6)	2309 (4)	57 (3)
C(2*m*)	−1025 (16)	1510 (6)	4107 (13)	56 (3)
O(1)	1858 (9)	155 (4)	5705 (7)	
O(2)	4208 (12)	70 (4)	7608 (9)	
O(3)	1839 (11)	4505 (4)	5029 (7)	
N(1)	3484 (11)	1807 (4)	4466 (8)	
N(2)	4085 (13)	3343 (5)	5436 (9)	
C(1)	3341 (14)	335 (6)	6484 (11)	39 (2)
C(2)	4200 (14)	968 (5)	5977 (10)	37 (2)
C(3)	3828 (15)	1593 (6)	6800 (11)	45 (2)
C(4)	4292 (14)	2270 (5)	6346 (11)	41 (2)
C(5)	3157 (15)	2787 (6)	5681 (11)	46 (2)
C(6)	5861 (13)	3195 (5)	5896 (10)	40 (2)
C(7)	7294 (15)	3607 (6)	5853 (11)	47 (2)
C(8)	8943 (17)	3327 (7)	6466 (12)	56 (3)
C(9)	9214 (17)	2664 (6)	7085 (13)	55 (3)
C(10)	7768 (14)	2267 (6)	7089 (11)	42 (2)
C(11)	6085 (13)	2537 (5)	6507 (10)	39 (2)

Hydrogen atoms found from the difference map

H(N1*a*)	4041	772	3810
H(N1*b*)	4170	1639	4606
H(N2)	3567	3780	5299
H(O3*a*)	995	4589	4119
H(O3*b*)	1439	4612	5655

applied. The final data set consisted of 2454 independent reflections of which 162 for which $I < 3\sigma(I)$ were rejected. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares calculations (Sheldrick, 1976). The C–H hydrogen atom coordinates were estimated geometrically (with C–H = 1·08 Å assumed) and for refinement allowed to ride (Sheldrick, 1976) on their respective C atom coordinates. The N–H and O–H hydrogen atom positions were obtained from a $(F_o - F_c)$ synthesis. Neutral-atom scattering factors were used (Cromer & Mann, 1968), those for Tl being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) (Cromer, 1965).

For the final stages of refinement the Tl, N and O atoms were allowed to assume anisotropic thermal parameters. In the final cycle the mean shift/σ was 0·001 and the maximum 0·004. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}044$, and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0{\cdot}047$, where $w = (\sigma^2|F_o| + n|F_o|^2)^{-1}$ with $n = 2{\cdot}01 \times 10^{-3}$. The final difference map showed maxima and minima of electron density of 2·89 and −2·02 e Å^{-3} near the Tl atom; these were attributed to the lack of an absorption correction. No other peak had an integrated electron density > 1e. The final atomic parameters are listed in Table 1.*

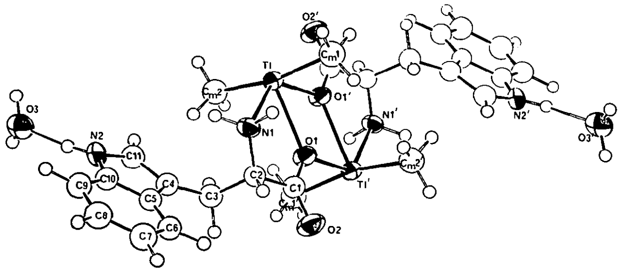


Fig. 1. Thermal ellipsoids (50% probability) and atomic labelling for $(CH_3)_2Tl(DL\text{-}TRP).H_2O$.

Discussion. A view of the complex with the atomic labelling is given in Fig. 1. The principal bond lengths and angles are listed in Table 2. The complex exists as a discrete dimer in which the $(CH_3)_2Tl$ unit is bonded to one N and two O atoms. The coordination about the Tl

Table 2. *Interatomic distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

Symmetry code

(i) $-x, -y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

(*a*) Thallium geometry

Tl–C(1*m*)	2·106 (14)	C(1*m*)–Tl–C(2*m*)	165·7 (4)
Tl–C(2*m*)	2·120 (13)	C(1*m*)–Tl–O(1)	91·5 (4)
Tl–O(1)	2·468 (6)	C(1*m*)–Tl–N(1)	94·9 (4)
Tl–N(1)	2·659 (8)	C(2*m*)–Tl–O(1)	100·9 (4)
		C(2*m*)–Tl–N(1)	96·8 (4)
		O(1)–Tl–N(2)	64·3 (2)
Tl–O(1^{i})	2·593 (8)	C(1*m*)–Tl–O(1^{i})	88·2 (4)
Tl···Tl^{i}	4·132	C(2*m*)–Tl–O(1^{i})	89·4 (4)
Tl···N(2^{ii})	3·434	O(1)–Tl–O(1^{i})	70·6 (2)
N(2)···O(3)	2·838	N(1)–Tl–O(1^{i})	134·8 (2)
		Tl–O(1)–Tl^{i}	109·4 (2)

(*b*) Hydrogen bonding

H(N2)···O(3)	1·933
H(O3*a*)···O(2^{ii})	1·851
H(O3*b*)···O(2^{iii})	2·143

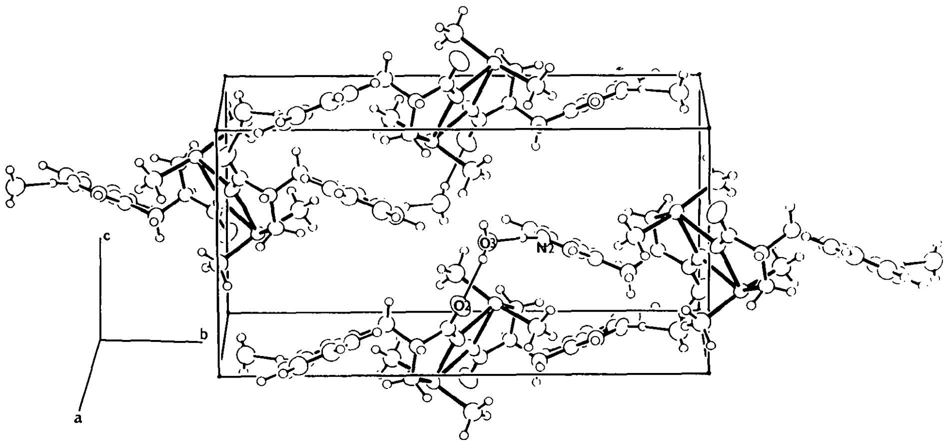


Fig. 2. View of crystal packing in $(CH_3)_2Tl(DL\text{-}TRP).H_2O$. The hydrogen bonds between O(2), O(3) and N(2) are labelled. The view is drawn in the monoclinic space group $P2_1/n$.

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* Lists of structure factors, anisotropic temperature factors and bond lengths and angles in the amino acid residue have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33171 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

atom is irregular and may be derived from a distorted octahedral complex with a vacant coordination site. The nearest neighbour of the Tl atom on the side distant from the N and two O atoms is the pyrrole N atom of an adjacent dimer (Tl···N = 3·43 Å). The Tl atom has no other contacts shorter than 4·0 Å with atoms outside its own dimer. The $(CH_3)_2Tl$ unit is nearly linear with C—Tl—C = 165°. With no significant close contacts to the Tl atom in the crystal, the large C—Tl—C angle cannot be explained by intermolecular interactions. The vacant coordination site and the observation that all the identifiable bonds lie on one side of the Tl atom suggest that the large C—Tl—C angles are due to internal bonding factors. Similar characteristics were found for both the dimeric $[(CH_3)_2TlX]_2$ derivatives (where X is a good bridging group leading to dimer formation) (Burke, Gray, Hayward, Matthews, McPartlin & Gillies, 1977) and the polymeric $[(\text{alkyl})_2TlX]_n$ derivatives (Chow & Britton, 1975*a*,*b*,*c*; Milburn & Truter, 1967).

The Tl—C lengths are in the range found for Tl—C bonds in similar $(CH_3)_2Tl^+$ dimer species, 2·11 to 2·20 Å (Chow & Britton, 1975*a*,*b*,*c*; Burke *et al.*, 1977), but the Tl—O lengths are significantly longer than the 2·36 to 2·40 Å found for Tl^{III} phenoxide derivatives (Burke *et al.*, 1977). The Tl—N length of 2·66 (1) Å is also longer than the Tl—N distances of 2·46 and 2·57 Å from pyridyl N atoms (Deacon, Faulks, Gatehouse & Jozsa, 1977). The ligand dimensions in the [DL-TRP] residue in $(CH_3)_2Tl$[DL-TRP] do not differ significantly from those found for TRPH.HBr (Takigawa, Ashida, Sasada & Kakudo, 1966) or for TRPH formate (Bye, Mostad & Rømming, 1973).

There are three hydrogen bonds involving the H_2O molecule (Table 2) which serve to link the dimer units into infinite chains (Fig. 2) and to tie adjacent dimer chains together.

The ^1H NMR spectrum of $(CH_3)_2Tl$(DL-TRP) in aqueous solution (pH 7) shows a value of 420 ± 2Hz for $^2J(^{205}Tl-^1H)$. This is close to the values of $^2J(^{205}Tl-^1H)$ found for other $(CH_3)_2TlX$ derivatives in aqueous solution (Burke, Matthews & Gillies, 1976).

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mer-cis(*N*)-*cis*(*O*)-Bis(glycinato)aminoethanolatocobalt(III) Hydrate

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Abstract. Racemic *mer-cis*(*N*)-*cis*(*O*)-$[Co(NH_2CH_2COO)_2(NH_2CH_2CH_2O)].H_2O$, FW 285·1, monoclinic, $P2_1/n$, $Z = 4$, $a = 9{\cdot}687$ (3), $b = 11{\cdot}957$ (3), $c = 9{\cdot}629$ (3) Å, $\beta = 103{\cdot}75$ (2)°, $U = 1083$ Å^3; μ(Mo $K\alpha$) ($\lambda = 0{\cdot}71069$ Å) = 16·7 cm^{-1}; $D_m = 1{\cdot}746$, $D_x = 1{\cdot}748$ g cm^{-3}. Block-diagonal least-squares calculations based on 2544 independent counter intensities reduced the R factor to 0·041. The average Co—O-