with K—O distances between 2·64 and 2·88 Å. In the crystal structure of the $\frac{5}{3}$ hydrate of potassium 5-ethylbarbiturate (Gartland, Gatehouse & Craven, 1975) the range of seven K—O distances is 2·67 to 3·02 Å. In potassium glyconate monohydrate (Panagiotopoulos, Jeffery, La Placa & Hamilton, 1974) eight nearest-neighbour O atoms are in the range of distances 2·61 to 3·24 Å.

The projection of the crystal structure along **b** is shown in Fig. 3. The short K—O distances, K—K contacts and other significant distances are given in Table 3. The molecules, stacked in layers parallel to (100), are linked to each other through strong K—O and weak van der Waals bonds.

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References

Biswas, A. B. & Ranade, A. C. (1967). Proc. 1st Int. Conference on Spectroscopy, Bombay, Vol. 2, pp. 348–352.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee. The CDC-3600 version incorporates modifications by W. C. Hamilton, J. A. Ibers, K. Johnson & S. Srikant.

Gartland, G. L., Gatehouse, B. M. & Craven, B. M. (1975). *Acta Cryst.* B**31**, 203–211.

Hine, J. & Haworth, H. W. (1958). *J. Am. Chem. Soc.* **80**, 2274–2275.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

Lingafelter, E. C. & Donohue, J. (1966). *Acta Cryst.* **20**, 321.

Panagiotopoulos, N. C., Jeffery, G. A., La Placa, S. J. & Hamilton, W. C. (1974). *Acta Cryst.* B**30**, 1421–1430.

Phillips, D. C. (1954). *Acta Cryst.* **7**, 746–751.

Rae, A. D. (1965). *Acta Cryst.* **19**, 683–684.

Rae, A. D. & Blake, A. B. (1966). *Acta Cryst.* **20**, 586.

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(L-Phenylalaninato)dimethylthallium(III)

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Abstract. $C_{11}H_{16}NO_2Tl$, $M_r = 398·3$, triclinic, $P1$, $a = 11·278$ (2), $b = 9·354$ (3), $c = 6·231$ (2) Å, $\alpha = 105·53$ (4), $\beta = 78·75$ (3), $\gamma = 103·66$ (2)°, $U = 609·3$ Å^3, $Z = 2$, $D_c = 2·17$ g cm^{-3}, μ(Mo $K\alpha$) = 127 cm^{-1}, $F(000) = 372$. The complex, $(CH_3)_2Tl$(L-PHE), in the crystal consists of two independent polymeric chains of $(CH_3)_2Tl$(L-phenylalanine) units linked by the carboxyl groups [Tl—C = 2·06 (2), 2·15 (2); Tl—O = 2·65 (1), 2·63 (1); Tl—N = 2·53 (1) and Tl$^{\text{i}}$—C = 2·17 (2), 2·09 (2); Tl$^{\text{i}}$—O = 2·66 (1), 2·54 (1); Tl$^{\text{i}}$—N = 2·53 (1) Å]. Each independent Tl atom is approximately octahedrally coordinated with the sixth coordination site in each case occupied by a bridging carboxyl O atom of an adjacent polymeric chain [Tl—O = 3·13, 3·06 Å].

Introduction. Small, colourless irregular needles were obtained by crystallization from water. Unit-cell and intensity data were measured on a Philips PW 1100 automatic four-circle diffractometer with Mo $K\alpha$ radiation, a graphite monochromator and the θ–2θ scan technique (Henrick, Matthews & Tasker, 1978). Complete data sets were recorded for two crystals with $3 \leq \theta \leq 30°$. Both crystals were *ca* 0·07 × 0·25 × 0·15 mm. There were no easily identifiable faces. For each data set the intensities of three standard reflections measured every 3 h decreased by *ca* 30% during data collection and were used to scale the data in each set to a common level. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. The data sets consisted of 2443 and 3122 independent reflections respectively and were merged through common reflections by linear least squares (Rae & Blake, 1966) to give 3204 unique reflections (interlayer scale factors of 1·0011 and 0·9989 respectively), of which 18 with $I \leq 3\sigma(I)$ were considered to be unobserved. The Patterson function and an initial difference map were solved in the space group $P\bar{1}$ and gave all the non-hydrogen atom positions but with a second phenyl ring ghosted above a complete $(CH_3)_2Tl$(L-PHE) molecule. The structure was refined from the centrosymmetrically related metal–ligand positions and the noncentrosymmetrically related

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phenyl-ring positions in the space group $P1$, by full-matrix least-squares calculations (Sheldrick, 1976). Neutral-atom scattering factors were used (Cromer & Mann, 1968), those for Tl being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) (Cromer, 1965).

The H atom coordinates were estimated geometrically (C—H = 1·08 Å) and for refinement were allowed to ride on their respective C atoms (Sheldrick, 1976). The Tl atoms were given anisotropic thermal parameters, and the phenyl rings were treated as rigid bodies (C—C = 1·395 Å).

It was necessary to constrain isotropic thermal parameters to be equal for chemically equivalent atoms in the two formula units. Based on the above restrictions (with the two intense reflections 200 and $\bar{2}00$, judged to be suffering from severe extinction, deleted from the data set), for the observed reflections, $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was 0·0421. The bond lengths and isotropic thermal parameters for this model were chemically reasonable with the exception of the N—C(2) lengths which were found to be 1·66 and 1·35 Å in the two independent molecules. The chemically equivalent distances in the two amino acid residues were then constrained to be equal within an e.s.d. of 0·01 Å by the addition of extra observational equations to the least-squares matrix (Sheldrick, 1976). The bond lengths were initially set at the average values obtained from the previous model and chemically reasonable distances and angles were then obtained at the completion of refinement. The final R was 0·0418 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0·0444 where $w = 1{\cdot}4071(\sigma^2|F_o| + 0{\cdot}001271|F_o|^2)^{-1}$. The mean and maximum shift/σ were 0·097 and 0·925 respectively. The two data sets were recombined to give the enantiomorph of the correct relative hand for L-phenylalanine (Gurskaya, 1964). A difference synthesis showed two peaks around each Tl atom with maximum and minimum electron densities of 3·54 and −3·15 e Å^{-3}, attributed to the absence of absorption correction. No other peak had an integrated electron density greater than 0·8 e. The final atomic parameters are listed in Table 1.*

Table 1. *Final fractional coordinates* (Tl ×10^5, *others* ×10^4) *and isotropic thermal parameters* (×10^3) *for* (L-*phenylalaninato*)*dimethylthallium*(III) (*e.s.d.'s in parentheses*)

	x	y	z	U (Å^2)
Molecule *A*				
Tl(*a*)	−2566	−12660	−30334	
O(1*a*)	−487 (12)	−1786 (12)	1221 (45)	52 (15)
O(2*a*)	−944 (10)	−3538 (14)	3284 (19)	52 (17)
N(*a*)	−1139 (11)	−4244 (15)	−2389 (18)	37 (13)
C(1*a*)	−995 (12)	−3046 (13)	1608 (20)	43 (19)
C(2*a*)	−1842 (11)	−4058 (12)	−99 (19)	38 (18)
C(3*a*)	−2480 (12)	−5565 (14)	418 (23)	49 (21)
C(4*a*)	−3490 (9)	−6514 (9)	−1019 (18)	44 (19)
C(5*a*)	−3873 (9)	−5997 (9)	−2624 (18)	56 (25)
C(6*a*)	−4754 (9)	−6939 (9)	−3931 (18)	64 (29)
C(7*a*)	−5254 (9)	−8398 (9)	−3632 (18)	63 (28)
C(8*a*)	−4871 (9)	−8915 (9)	−2028 (18)	81 (44)
C(9*a*)	−3989 (9)	−7973 (9)	−721 (18)	62 (28)
C(1*ma*)	1590 (17)	−1661 (22)	−3372 (35)	54 (25)
C(2*ma*)	−2023 (17)	−979 (22)	−2457 (34)	54 (25)
Molecule *B*				
Tl(*b*)	2583 (8)	16249 (8)	30402 (14)	
O(1*b*)	336 (12)	1885 (12)	−1142 (26)	
O(2*b*)	545 (10)	3541 (13)	−3255 (19)	
N(*b*)	932 (11)	4294 (16)	2460 (18)	
C(1*b*)	725 (12)	3158 (13)	−1563 (20)	
C(2*b*)	1389 (10)	4472 (13)	136 (19)	
C(3*b*)	2743 (11)	4439 (16)	−590 (24)	
C(4*b*)	3625 (10)	5694 (9)	824 (18)	
C(5*b*)	4085 (10)	5369 (9)	2525 (18)	
C(6*b*)	4900 (10)	6485 (9)	3791 (18)	
C(7*b*)	5255 (10)	7925 (9)	3358 (18)	
C(8*b*)	4794 (10)	8250 (9)	1657 (18)	
C(9*b*)	3979 (10)	7134 (9)	391 (18)	
C(1*mb*)	−1702 (17)	1667 (22)	3729 (34)	
C(2*mb*)	1981 (17)	1069 (23)	2824 (33)	

Discussion. This work is part of a study of the chemistry of dialkylthallium amino acid derivatives which was undertaken in the hope that the structural data would indicate the factors influencing the observed NMR parameters.

A perspective view of one of the independent formula units of $(CH_3)_2Tl(L\text{-}PHE)$, with the crystallographic numbering scheme, is shown in Fig. 1. The principal bond lengths and angles are listed in Table 2. The $(CH_3)_2Tl(L\text{-}PHE)$ units are linked into polymeric chains *via* O bridging and these chains are held together by weak Tl—O interactions (Fig. 2). Each Tl atom is six-

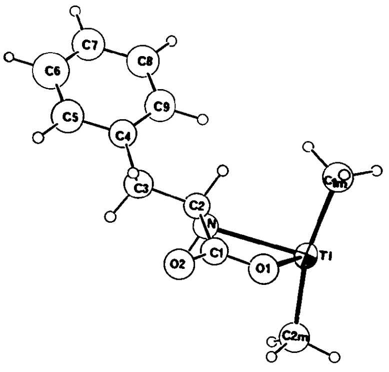

Fig. 1. Thermal ellipsoids (50% probability) and atomic labels for $(CH_3)_2Tl(L\text{-}PHE)$, molecule A.

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles in the amino acid residue have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33274 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Frairs, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses, in the coordination sphere of the title compound*

Tl(*a*)—C(1*ma*)	2·060 (19)	Tl(*b*)—C(1*mb*)	2·176 (18)
Tl(*a*)—C(2*ma*)	2·152 (19)	Tl(*b*)—C(2*mb*)	2·098 (20)
Tl(*a*)—O(1*a*)	2·655 (15)	Tl(*b*)—O(1*b*)	2·665 (15)
Tl(*a*)—N(*a*)	2·527 (13)	Tl(*b*)—N(*b*)	2·534 (13)
Tl(*a*)—O(2*a*$^{\text{i}}$)	2·629 (12)	Tl(*b*)—O(2*b*$^{\text{i}}$)	2·539 (12)
Tl(*a*)···O(1*b*)	3·130	Tl(*b*)···O(1*a*)	3·056
Tl(*a*)···N(*b*$^{\text{ii}}$)	4·414	Tl(*b*)···N(*a*$^{\text{iii}}$)	4·556
Tl(*a*)···Tl(*b*)	4·213	Tl(*a*)···Tl(*b*$^{\text{i}}$)	4·259
Tl(*a*)···Tl(*a*$^{\text{i}}$)	6·231	Tl(*b*)···Tl(*b*$^{\text{i}}$)	6·231

Table 2 (*cont.*)

C(1*ma*)—Tl(*a*)—C(2*ma*)	165·6 (8)	C(1*mb*)—Tl(*b*)—C(2*mb*)	163·7 (8)
C(1*ma*)—Tl(*a*)—O(1*a*)	89·1 (6)	C(1*mb*)—Tl(*b*)—O(1*b*)	90·5 (6)
C(1*ma*)—Tl(*a*)—N(*a*)	98·8 (6)	C(1*mb*)—Tl(*b*)—N(*b*)	95·3 (6)
C(2*ma*)—Tl(*a*)—O(1*a*)	91·2 (6)	C(2*mb*)—Tl(*b*)—O(1*b*)	100·8 (6)
C(2*ma*)—Tl(*a*)—N(*a*)	94·4 (6)	C(2*mb*)—Tl(*b*)—N(*b*)	100·2 (6)
O(1*a*)—Tl(*a*)—N(*a*)	65·9 (4)	O(1*b*)—Tl(*b*)—N(*b*)	64·6 (3)
O(1*a*)—Tl(*a*)—O(2*a*$^{\text{i}}$)	134·0 (4)	O(1*b*)—Tl(*b*)—O(2*b*$^{\text{i}}$)	133·2 (4)
N(*a*)—Tl(*a*)—O(2*a*$^{\text{i}}$)	68·4 (4)	N(*b*)—Tl(*b*)—O(2*b*$^{\text{i}}$)	68·8 (3)
C(1*ma*)—Tl(*a*)—O(2*a*$^{\text{i}}$)	102·9 (6)	C(1*mb*)—Tl(*b*)—O(2*b*$^{\text{i}}$)	89·2 (6)
C(2*ma*)—Tl(*a*)—O(2*a*$^{\text{i}}$)	80·2 (5)	C(2*mb*)—Tl(*b*)—O(2*b*$^{\text{i}}$)	91·6 (6)
O(1*a*)—Tl(*a*)—O(1*b*)	85·3 (4)	O(1*b*)—Tl(*b*)—O(1*a*)	86·7 (4)
N(*a*)—Tl(*a*)—O(1*b*)	149·8 (4)	N(*b*)—Tl(*b*)—O(1*a*)	151·2 (4)
C(1*ma*)—Tl(*a*)—O(1*b*)	89·4 (4)	C(1*mb*)—Tl(*b*)—O(1*a*)	86·7 (4)
C(2*ma*)—Tl(*a*)—O(1*b*)	76·3 (4)	C(2*mb*)—Tl(*b*)—O(1*a*)	82·3 (6)
O(2*a*$^{\text{i}}$)—Tl(*a*)—O(1*b*)	137·9 (6)	O(2*b*$^{\text{i}}$)—Tl(*b*)—O(1*a*)	140·0 (4)
Tl(*a*)—O(1*a*)—Tl(*b*)	94·8 (3)	Tl(*a*)—O(1*b*)—Tl(*b*)	92·9 (3)

Symmetry code: (i) $x, y, 1-z$; (ii) $x, 1-y, 1-z$; (iii) $x, 1+y, 1-z$.

coordinate with the Tl—O contacts between the two independent polymer chains considerably more ionic than those within each chain. The bridging Tl—O distances (3·13, 3·06 Å) are only marginally bonding when compared with the sum of the van der Waals radii for Tl (1·96 Å, Bondi, 1964) and O (1·40 Å, Grdenić, 1965). The irregular geometry of the donor atoms about the Tl atoms may be derived from a distorted pentagonal bipyramid with one equatorial coordination site vacant. The nearest contact to the Tl atom on the side of the vacant coordination site is an adjacent Tl atom at 4·259 Å (Fig. 2). The Tl—C and Tl—N lengths are similar to the corresponding values found in $(CH_3)_2$Tl(DL-TRP) (Henrick, Matthews & Tasker, 1978).

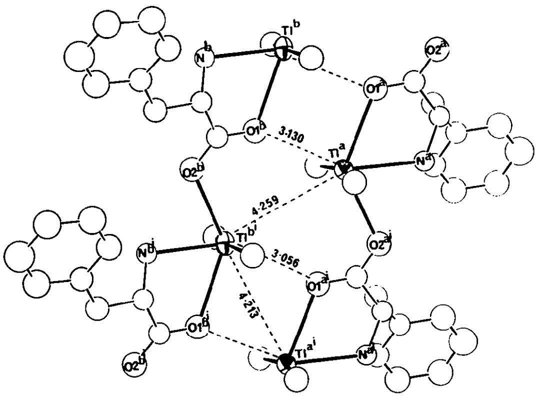

Fig. 2. View of the polymer interactions between the two formula units of $(CH_3)_2$Tl(L-PHE) per equivalent position. The superscript (i) indicates a translation of $-x, -y, 1-z$.

The four-membered Tl_2O_2 ring in the polymeric $(CH_3)_2$Tl(L-PHE) is of a similar geometry to the ring found in the dimeric $(CH_3)_2$Tl(DL-TRP) but differs from the corresponding ring found in polymeric $(CH_3)_2$Tl(OAc) (Chow & Britton, 1975). In the latter, the carboxyl ligand is bidentate to the Tl atom.

The distances and angles within the coordinated amino acid are similar to the values found for L-PHE.HCl (Gurskaya, 1964).

The two independent C—Tl—C angles of 163·7 (8) and 165·6 (8)° do not differ significantly from the corresponding value of 165·4 (7)° found for $(CH_3)_2$Tl(DL-TRP) (Henrick, Matthews & Tasker, 1978). For both $(CH_3)_2$Tl(L-PHE) and $(CH_3)_2$Tl(DL-TRP) one of the angles between the equatorial donor atoms is restricted by the geometry of the ligand to a value considerably less than 90°. As a result the Tl atom in each case experiences an asymmetric environment of charges from the electrostatic Tl—O and Tl—N bonds. The bending of the methyl C atoms away from the chelate ring may be described in terms of charge repulsions between the highly covalent Tl—C bonds and the more polar equatorial bonds. The distortion from linearity in these complexes is similar to that found in other $(CH_3)_2$Tl complexes containing a chelating ligand where the $(CH_3)_2Tl$ group has an asymmetric distribution of equatorial charges. This departure from linearity of the $(CH_3)_2Tl$ group is approximately independent of the size of the chelate ring, as evident from the angles found for the following derivatives: tropolonate 166·9 (9)°, acetylacetonate 170·0 (20)°, and acetate 171·8 (16)° (Chow & Britton, 1975), 1,10-phenanthroline 168·3 (15)° (Blundell & Powell, 1972), and for several phenoxide and thiophenoxide dimeric species, 173 (3), 166·2 (10) and 163·5 (9)° (Burke, Gray, Hayward, Matthews, McPartlin & Gillies, 1977).

The ^1H NMR spectrum of $(CH_3)_2Tl$(L-PHE) in aqueous solution (pH 7) shows a value of 413 ± 2 Hz for $^2J(^{205}Tl-^1H)$, similar to the ~420 Hz found for $(CH_3)_2TlY$ (Y = anionic species) in aqueous solutions (Burke, Matthews & Gillies, 1976; Gillies, Hoad, Matthews & Thakur, 1977).

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References

Blundell, T. L. & Powell, H. M. (1972). *Proc. R. Soc. London Ser. A*, **331**, 161–169.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Burke, P. J., Gray, L. A., Hayward, P. J. C., Matthews, R. W., McPartlin, M. & Gillies, D. G. (1977). *J. Organomet. Chem.* **136**, C7–C10.
Burke, P. J., Matthews, R. W. & Gillies, D. G. (1976). *J. Organomet. Chem.* **118**, 129–134.
Chow, Y. M. & Britton, D. (1975). *Acta Cryst.* B**31**, 1929–1934.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Gillies, D. G., Hoad, C. S., Matthews, R. W. & Thakur, M. M. (1977). *J. Organomet. Chem.* **124**, C31–C36.
Grdenić, D. (1965). *Q. Rev. Chem. Soc.* **19**, 303–328.
Gurskaya, G. V. (1964). *Kristallografiya*, **9**, 839–845.
Henrick, K., Matthews, R. W. & Tasker, P. A. (1978). *Acta Cryst.* B**34**, 935–937.
Rae, A. D. & Blake, A. B. (1966). *Acta Cryst.* **20**, 586.
Sheldrick, G. M. (1976). *SHELX* programs. Univ. of Cambridge, England.

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Structure of Disodium Malonate Monohydrate

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Abstract. $Na_2C_3H_2O_4.H_2O$, M_r = 167·0, is orthorhombic, space group $Pbc2_1$, with a = 7·7486 (8), b = 12·6419 (17), c = 5·7866 (6) Å, V = 566·84 Å^3, Z = 4. Each Na^+ ion is surrounded by six O atoms forming distorted octahedra. The polyhedra form a two-dimensional network perpendicular to **a**, by sharing faces, edges and corners. These networks are linked along **a** through carboxylate bridges. The malonate ion has a conformation which imposes a distortion of the C–C–C angle to 114·9 (2)°.

Introduction. Weissenberg photographs revealed the Laue class *mmm*. The systematic absences $0kl$, $k \neq 2n$ and $h0l$, $l \neq 2n$ gave $Pbc2_1$ and $Pbcm$ as possible space groups. The non-centrosymmetric $Pbc2_1$ was chosen (indicated by E statistics). Cell dimensions were obtained by least squares from powder spectra obtained with a Guinier–Hägg focusing camera (Cu $K\alpha_1$ radiation, λ = 1·54056 Å, 22 °C). Al (cubic, a = 4·04934 Å) was used as internal standard. A four-circle diffractometer (CAD-4) was used in the data collection. Table 1 gives details of the collection and reduction of the intensities and the refinement. During data collection three standard reflexions were checked after every 50 measurements. No systematic variations in their intensities were observed. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects [$\sigma_c(I)$ is based on counting statistics]. The expression $p = (\cos^2 2\theta + \cos^2 2\theta_M)/(1 + \cos^2 2\theta_M)$ was used in the correction of the polarization effects. θ_M is the Bragg angle for the monochromator.

The positions of the non-hydrogen atoms were determined with *MULTAN* (Germain, Main & Woolfson, 1971). The parameters were refined by full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, with weights $w^{-1} = \sigma_c^2/4|F_o|^2 + C|F_o|^2$. C was adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2\rangle$ were obtained in different $|F_o|$ and $\sin\theta$ intervals. The origin was kept fixed along **c** by not refining the z parameter of Na(1). The positions of the H atoms were obtained from a