

Fig. 3. The molecular shape. (Distances in Å.)

Cationomycin is of particular interest because of the exceptionally low toxicity to mice compared with other ionophore antibiotics (ID_0 200 mg kg^{-1} , intraperitoneal). In this respect, the role of the aromatic acyl tail in the biological activity may be worth further study.

Calculations were performed on a FACOM 230-75 computer of this Institute using the UNICS III program system (Sakurai & Kobayashi, 1979).

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Thallium Triacetate Monohydrate*

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Abstract. $Tl[C_2H_3O_2]_3 \cdot H_2O$, monoclinic, $P2_1/c$, $a = 9.311$ (4), $b = 14.341$ (6), $c = 9.198$ (2) Å, $\beta = 119.69$ (2)°, $V = 1067.0$ Å³, $M_r = 399.5$, $Z = 4$, $D_x = 2.49$ Mg m⁻³, $\mu = 15.11$ mm⁻¹. The structure was refined by X-ray diffraction to $R = 0.04$ for 577 observed reflections. The Tl atom is irregularly coordinated by eight O atoms (Tl-O = 2.17-2.78 Å). The angles between adjacent bonds correlate with the strengths of the bonds. The molecules are linked by a bridging acetate O atom and a hydrogen bond into columns running along c . There is a simple relation between the structure of the monohydrate and the anhydrous triacetate.

Introduction. Thallium triacetate monohydrate was prepared by dissolving 0.2 g of $Tl[CH_3CO_2]_3$ (Alfa Products) in 10 ml distilled water and leaving it uncovered at room temperature. Large colourless plates of the title compound appeared after several days. Since the crystals decomposed in a few hours when removed from the solution, the crystal used was ground to a cylinder and sealed in a Lindemann-glass capillary. The structure was determined by X-ray diffraction, experimental details being given in Table 1. When the structure had been fully refined with anisotropic temperature factors for Tl the largest positive and negative peaks in the residual electron density map were found in the neighbourhood of the Tl atom and were identified as arising from anisotropic extinction. Consequently the 15 strongest reflections were omitted

* catena- μ -Acetato-O, μ -O'-aquadiacetatothallium(III).

Table 1. Summary of structure determination

Crystal shape and size	Cylinder of radius 0.10 mm and length 0.3 mm along [11 $\bar{2}$]
Diffractometer	Nicolet P ₂
Radiation and wavelength	Graphite-monochromatized Mo K α , $\lambda = 0.71069 \text{ \AA}$
Reflections used for measuring lattice parameters	15
Absorption correction applied (max. and min.)	10.7 ($2\theta = 0^\circ$), 9.6 ($2\theta = 35^\circ$)
Temperature	293K
Max. 2θ measured	35°
Standard reflections	233, 114, e.s.d. 1.2%
Number of intensity measurements	836
Number of unique reflections	655
$R_1 = (\sum F_o - F_c) / \sum F_o $	0.038 for 655 reflections
$R_2 = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.043
R_1 for 15 strongest reflections with $w = 0$	0.048
Weighting scheme	$w = (\sigma^2_{\text{counting}} + 0.03 F_o^2)^{-1}$ $w = 0$ for 63 unobserved reflections with $F_c < F_o$ and for the 15 strongest reflections.
Error in an observation of unit weight	1.18
Average, maximum (shift/error)	0.4, 2.0 [z(H41)]
Final difference synthesis:	
maximum	+ 1 e \AA^{-3} in neighbourhood
minimum	- 2 e \AA^{-3} of Tl atom
Isotropic secondary-extinction correction (Larson, 1967)	$g = 2.8 \times 10^{-5}$
$F(000)$	736
Scattering factors	International Tables for X-ray Crystallography (1962) Table 3.3.1A (O,C,H) and Table 3.3.1B (Tl) corrected for anomalous dispersion (Table 3.3.2C)

Table 2. Atomic parameters for $\text{Tl}[\text{CH}_3\text{CO}_2]_3 \cdot \text{H}_2\text{O}$ ($\times 10^4$ except H $\times 10^3$)

	x	y	z	$U (\text{\AA}^2)$
Tl	3249 (1)	3180 (1)	4786 (1)	*
O(W)	2876 (15)	4233 (10)	2636 (18)	390 (40)
O(1)	4473 (16)	4626 (9)	6370 (16)	490 (40)
O(2)	1920 (17)	4196 (9)	5561 (16)	470 (40)
O(3)	2341 (19)	1627 (9)	4750 (20)	550 (40)
O(4)	759 (17)	2591 (11)	2805 (17)	490 (40)
O(5)	5723 (15)	2752 (9)	5391 (16)	390 (40)
O(6)	4247 (16)	2280 (9)	2764 (16)	350 (30)
C(1)	3107 (29)	4749 (15)	6327 (29)	430 (60)
C(2)	2872 (37)	5566 (24)	7241 (40)	840 (100)
C(3)	1015 (27)	1819 (15)	3427 (28)	440 (60)
C(4)	-282 (38)	1054 (19)	2617 (40)	690 (90)
C(5)	5594 (25)	2297 (14)	4056 (26)	350 (40)
C(6)	7150 (31)	1907 (15)	4260 (32)	480 (80)
H(1)	325 (31)	375 (18)	175 (35)	90
H(2)	380 (37)	442 (21)	332 (40)	90
H(21)	376 (33)	616 (18)	677 (35)	90
H(22)	233 (37)	543 (23)	699 (38)	90
H(23)	404 (33)	583 (18)	786 (35)	90
H(41)	-93 (37)	144 (19)	219 (37)	90
H(42)	25 (34)	71 (20)	227 (37)	90
H(43)	-15 (36)	61 (22)	333 (39)	90
H(61)	746 (33)	243 (19)	320 (37)	90
H(62)	691 (31)	116 (19)	325 (36)	90
H(63)	710 (37)	156 (22)	476 (41)	90

* Temperature factor for Tl = $\exp \{-2\pi^2 \times 10^{-4} [297 (9)h^2a^{*2} + 454 (9)k^2b^{*2} + 282 (8)l^2c^{*2} - 60 (10)hka^{*b^*} + 304 (12)hla^{*c^*} - 58 (10)klb^{*c^*}]\}$.

from the final refinement. Atomic coordinates are given in Table 2.*

Discussion. Selected bond distances and angles are given in Table 3. The structure of thallium triacetate monohydrate is related to the structure of the anhydrous triacetate (Faggiani & Brown, 1978) as shown in Fig. 1. In both, the metal is eight-coordinate with acetate O atoms bridging the molecules into columns

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36866 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected bond distances (\AA) and angles ($^\circ$)

Tl-O(1)	2.46 (1)	Tl-O(5)	2.17 (1)	
Tl-O(2)	2.24 (2)	Tl-O(6)	2.51 (2)	
Tl-O(3)	2.38 (1)	Tl-O(6')	2.78 (2)	
Tl-O(4)	2.29 (1)	Tl-O(W)	2.37 (2)	
	<i>a-b</i>	1-2	3-4	5-6
O(a)-C(a)		1.27 (3)	1.26 (2)	1.34 (3)
O(b)-C(a)		1.26 (3)	1.21 (3)	1.23 (2)
C(a)-C(b)		1.52 (5)	1.53 (3)	1.48 (4)
O(a)-C(a)-O(b)		121 (2)	122 (2)	119 (2)
O(a)-C(a)-C(b)		121 (2)	118 (3)	116 (2)
O(b)-C(a)-C(b)		118 (3)	120 (2)	126 (2)
O(a)-Tl-O(b)		55.4 (5)	55.2 (5)	51.4 (4)

Principal OH...O hydrogen bonds

	O-O	O-H	H...O	O-H-O
O(W)-H(1)-O(3)	2.74 (2)	1.2 (3)	1.7 (3)	138 (17)
O(W)-H(2)-O(1)	2.71 (2)	0.8 (2)	2.0 (3)	142 (29)

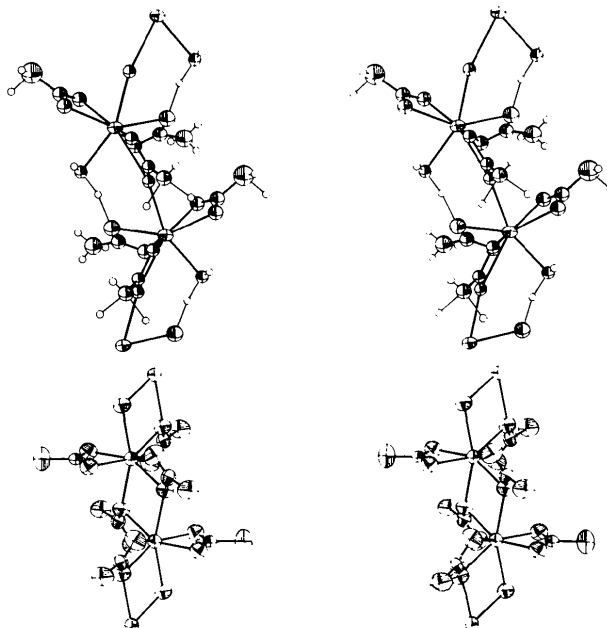


Fig. 1. Stereoscopic view of $\text{Tl}[\text{CH}_3\text{CO}_2]_3 \cdot \text{H}_2\text{O}$ (top) and $\text{Tl}[\text{CH}_3\text{CO}_2]_3$ (Faggiani & Brown, 1978) down a^* showing the linking into columns along the c axis (vertical).

running along the *c* direction. In the *a* and *b* directions the columns are arranged in a close-packed array. Adjacent molecules within the columns are related by the *c* glide plane but in the anhydrous triacetate there is also a crystallographic twofold axis through each molecule, and the molecules are linked by two Tl–O–Tl bridges. The structure of the hydrate can be formally derived from the anhydrous compound by inserting the water molecule into one of the Tl–O–Tl bridges to form a Tl–O...H–O–Tl bridge. This destroys the twofold symmetry and rotates the pseudo twofold axis of the molecule by about 30°. In the hydrate there is also hydrogen bonding between the water molecules of one column and an acetate of an adjacent column.

The Tl atoms, as in a number of other chelated complexes, are eight-coordinate but the coordination is remarkably irregular compared to other crystals in this series. The Tl–O bond lengths range from 2.17–2.78 Å and the angles do not correspond to any regular polyhedron. This irregularity can, however, be understood by considering the bonding constraints on the O atoms. We can assume that each acetate O atom forms bonds with a total bond valence (bond strength) of 0.5 valence units (v.u.), that the hydrogen bonds formed by the water molecule have the normal bond valence of 0.2 v.u. (Brown, 1978) and that, conse-

quently, the water will coordinate to Tl with a bond of valence $2 \times 0.2 = 0.4$ v.u. In order for the Tl to be eight-coordinate one acetate O atom must be bridging so that it is expected to form two bonds of $0.5/2 = 0.25$ v.u. Two acetate O atoms must also act as hydrogen-bond acceptors thus reducing the O–Tl bonds to a valence of $0.5 - 0.2 = 0.3$ v.u. Table 4 shows that, apart from the longest bond, the observed bond lengths are within 0.04 Å (r.m.s. deviation) of the values predicted by this model.

The irregular coordination around Tl provides a good opportunity to examine the relation between Tl–O bond lengths and O–Tl–O bond angles for those O atoms that are nearest neighbours. Such relations are well known for tetrahedrally coordinated species (Baur, 1970; Brown, 1973; Murray-Rust, Bürgi & Dunitz, 1978) but have been less well studied for other geometries. Following the procedure shown to be appropriate in previous studies (Brown, 1973; Murray-Rust *et al.*, 1978) the bond lengths were converted to bond valences. Fig. 2 shows the plot of bond angles against the average valence of the two defining Tl–O bonds in $\text{Tl}[\text{CH}_3\text{CO}_2]_3 \cdot \text{H}_2\text{O}$ and a number of other eight-coordinate Tl^{III} acetates. The angle between the chelating bonds in each case is about 55° but the other angles show a strong variation with average bond valence. The outlying point *A* represents the bond between the two bridging O atoms in $\text{Tl}[\text{CH}_3\text{CO}_2]_3$.

The H atoms are not well located but almost all individual C–H and O–H bond lengths are within two standard errors of 1.0 Å. The water molecule forms normal hydrogen bonds to O(1) and O(3) (Table 3) and many of the methyl H atoms have O neighbours in the range 2.5–3.2 Å which has been shown (Brown, 1980) to represent weak hydrogen bonding.

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Table 4. Prediction of Tl–O bond valence and lengths

	Bond valence (v.u.)*		Bond length (Å)	
	Predicted	Observed	Predicted	Observed
O(5) } simply bonded	0.50	0.61 (4)	2.24	2.17 (1)
O(2) } acetate O	0.50	0.50 (4)	2.24	2.24 (2)
O(4) } water	0.50	0.45 (3)	2.24	2.29 (1)
O(W) } hydrogen bond	0.40	0.36 (4)	2.33	2.37 (2)
O(3) } acceptors	0.30	0.35 (4)	2.44	2.38 (1)
O(1) } bridging	0.30	0.29 (3)	2.44	2.46 (1)
O(6) } O	0.25	0.26 (3)	2.52	2.51 (2)
O(6) } O	0.25	0.14 (4)	2.52	2.78 (2)

* Valences calculated using bond valence = (bond length/2.0)^{-6.0}.

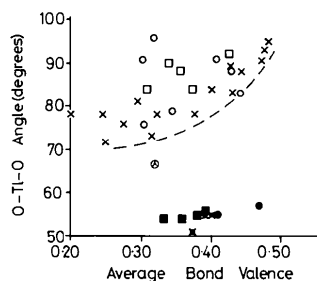


Fig. 2. O–Tl–O angles (°) versus the average valence (v.u.) of the two Tl–O bonds. \times = $\text{Tl}[\text{CH}_3\text{CO}_2]_3 \cdot \text{H}_2\text{O}$ (present work), \circ = $\text{Tl}[\text{CH}_3\text{CO}_2]_3$ (Faggiani & Brown, 1978), \square = $\text{Tl}[\text{Tl}(\text{CH}_3\text{CO}_2)_4]$ (Brown & Faggiani, 1980). Filled figures refer to the angle between chelating bonds. The point *A* refers to the angle between two bridging bonds. The dashed line is an arbitrary dividing line.

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