

Thallium(III) Trinitrate Trihydrate

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Abstract. $\text{Tl}(\text{NO}_3)_3(\text{H}_2\text{O})_3$ ($M_r = 444.25$, CAS No. 56050-12-5) is rhombohedral, space group $R\bar{3}$, $a = 11.821$ (6), $c = 10.889$ (4) Å, $Z = 6$, $V = 1317.7$ Å³, $D_c = 3.36$ g cm⁻³ (hexagonal setting). The Tl atom is nine coordinate, being chelated by three bidentate NO_3^- ions [Tl–O = 2.299 (8) and 2.637 (10) Å] and coordinated by three water molecules [Tl–O = 2.293 (7) Å] which are ideally placed for transfer to an organic substrate when thallium nitrate is used as an oxidant in solution.

Introduction. A spherical crystal ($r = 0.12$ mm) of $\text{Tl}(\text{NO}_3)_3(\text{H}_2\text{O})_3$ (Alfa Products 99%) was sealed in a thin-walled Lindemann capillary inside a dry box. Precession photographs showed rhombohedral symmetry with no systematic absences, indicating one of the space groups $R3$, $R\bar{3}$, $R32$, $R3m$, or $R\bar{3}m$. Accurate lattice parameters were obtained from a Syntex $P\bar{1}$ diffractometer by a least-squares fit to 15 well centred reflexions with $2\theta \geq 25^\circ$ [Mo $K\alpha$ radiation, $\lambda(K\alpha) = 0.71069$ Å]. The intensities of 2233 reflexions with $2\theta \leq 55^\circ$ were measured on the same diffractometer; of these, 1909 had intensities more than three standard errors above background. They were corrected for Lorentz, polarization and absorption (spherical correction with $\mu R = 2.3$) effects. Equivalent reflexions were averaged yielding 679 symmetry-independent intensities.

The space groups $R3m$ and $R\bar{3}m$ would require Tl to lie on positions of $3m$ symmetry and, as this was considered unlikely, these space groups were not considered further. A Patterson function gave the position of the Tl atom and a subsequent difference synthesis calculated in the space group $R\bar{3}$ revealed the positions of the N and O atoms. The structure was refined in $R\bar{3}$ using the full-matrix least-squares program *CUDLS* which minimized $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma_F^2 + (0.02F)^2]^{-1}$ except for reflexions with $F_c < F_o$ and $I < 3\sigma_I$ for which $w = 0$ (σ_I and σ_F are the standard errors in I and F , respectively, based on counting statistics). The free parameter in the weighting scheme was chosen to make $\langle w(|F_o| - |F_c|)^2 \rangle$ independent of F . The scattering factors for Tl, N and O were taken from Cromer & Waber (1965), the Tl factors being corrected for anomalous dispersion. H atoms were not included. This refinement gave a chemically plausible structure with $R_2 = 0.051$

$\{[\sum w(F_o - F_c)^2 / (N_r - N_p)]^{1/2} = 2.1\}$ but a model in space group $R32$ would not refine below $R_2 = 0.10$ and gave a chemically unlikely structure. No refinement was tried in $R3$ since it was not expected to reveal differences from the $R\bar{3}$ structure that would be significant. The largest features of a final difference synthesis were associated with the Tl atoms; the H atoms could not be seen.*

Discussion. The final atomic coordinates are given in Table 1. Bond lengths and angles are given in Table 2. $\text{Tl}(\text{NO}_3)_3(\text{H}_2\text{O})_3$ forms discrete molecules lying on the crystallographic threefold axis. The water and bidentate nitrate groups form a tricapped trigonal prismatic coordination around Tl in which the three equatorial distances are significantly longer (2.64 Å) than the distances to the corners of the prism (2.29 Å) (Fig. 1). The nitrate ion is significantly distorted from D_{3h} symmetry by the different bonding environments of the three O atoms. The thermal root mean square displacements of all atoms from their mean positions lie between 0.12 and 0.25 Å.

The molecules are linked by hydrogen bonds. The H atom positions in Table 1 have been chosen to give O–H distances of 0.94 Å and an H–O–H angle of 104° with one bond pointing to O(1). This H, H(1), then has five other O neighbours at distances between

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33339 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$)

	x	y	z
Tl	0	0	2392.1 (5)
N	7742 (9)	7866 (9)	1260 (7)
O(1)	6897 (9)	6958 (8)	654 (8)
O(2)	8945 (8)	8227 (9)	1109 (7)
O(3)	7471 (9)	8482 (9)	2020 (7)
O(4)	4947 (7)	7811 (8)	473 (6)
H(1)*	5620	8580	100
H(2)*	5357	7660	1134

* Inferred from chemical considerations only.

Table 2. Bond distances (Å), valences and angles (°) in $\text{Tl}(\text{NO}_3)_3(\text{H}_2\text{O})_3$

Bond valences (in square brackets) are given in valence units and are equal to $(\text{bond length}/R_0)^{-N}$ with $R_0 = 2.00$, $N = 6$ for Tl—O and $R_0 = 1.40$, $N = 4.6$ for N—O. H—O bond valences from Brown (1976).

		Nitrate ion					
Tl—O(4) × 3	2.293 (7)	[0.44]	N—O(1)	1.230 (11)	[1.81]	O(1)—N—O(2)	120 (1)
Tl—O(2) × 3	2.299 (8)	[0.43]	N—O(2)	1.274 (14)	[1.54]	O(1)—N—O(3)	122 (1)
Tl—O(3) × 3	2.637 (10)	[0.19]	N—O(3)	1.245 (15)	[1.71]	O(2)—N—O(3)	117 (1)
Total valence around Tl = 3.19			Total valence around N = 5.07				

Hydrogen bonds

O(4)—O(1)	2.812 (8)	H(1)—O(1)	1.86	[0.17]	O(4)—H(1)—O(1)	179
O(4)—O(3)	2.852 (13)	H(1)—O(3)*	2.50	[0.05]	O(4)—H(1)—O(3)	102
O(4)—O(2)	3.002 (10)	H(1)—O(2)	2.81	[0.02]	O(4)—H(1)—O(2)	92
O(4)—O(3)'	3.331 (10)	H(1)—O(3)'	2.92	[0.02]	O(4)—H(1)—O(3)'	107
O(4)—O(2)'	3.780 (10)	H(1)—O(2)'	3.06	[0.01]	O(4)—H(1)—O(2)'	134
O(4)—O(3)''	3.162 (13)	H(1)—O(3)''	3.07	[0.01]	O(4)—H(1)—O(3)''	87
O(4)—O(1)	2.948 (16)	H(2)—O(1)	2.41	[0.06]	O(4)—H(2)—O(1)	117
O(4)—O(3)	3.162 (13)	H(2)—O(3)	2.38	[0.06]	O(4)—H(2)—O(3)	141
O(4)—O(4)	3.106 (13)	H(2)—O(4)	2.41	[0.06]	O(4)—H(2)—O(4)	131
O(4)—O(4)'	3.106 (13)	H(2)—O(4)'	2.96	[0.01]	O(4)—H(2)—O(4)'	90

Total valence around O(1) 2.04; O(2) 2.00; O(3) 2.02; O(4) 2.04

* This O(3) is on the same molecule as H(1).

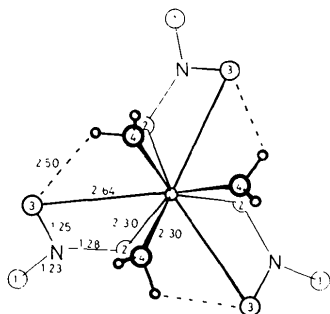


Fig. 1. Structure of the molecule of $\text{Tl}(\text{NO}_3)_3(\text{H}_2\text{O})_3$. O atoms are numbered. Small circles are Tl (at centre of molecule) and H.

2.5 and 3.2 Å (Brown, 1976). The second O—H points between three O atoms each lying about 3 Å from the water O [O(4)]. The bond valences (Brown & Shannon, 1973) calculated for this structure are given in Table 2, and the atomic valences obtained by summing these bond valences at each atom agree satisfactorily with the expected values, confirming the proposed hydrogen-bonding scheme.

$\text{Tl}(\text{NO}_3)_3(\text{H}_2\text{O})_3$ is important as an oxidant in organic synthesis (McKillop, 1975). The structure described here suggests that a key role is played in this reaction by the H_2O ligands. When Tl attacks a C—C double bond, the water O atoms are ideally placed for transfer directly to the C atoms. H(1) already forms an incipient hydrogen bond to O(3) and could easily be transferred to the nitrate group to give HNO_3 as the Tl is reduced. In methanol solution it is likely that the H_2O ligands would be replaced by HOCH_3 resulting in the addition of $-\text{OCH}_3$ instead of $-\text{OH}$.

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