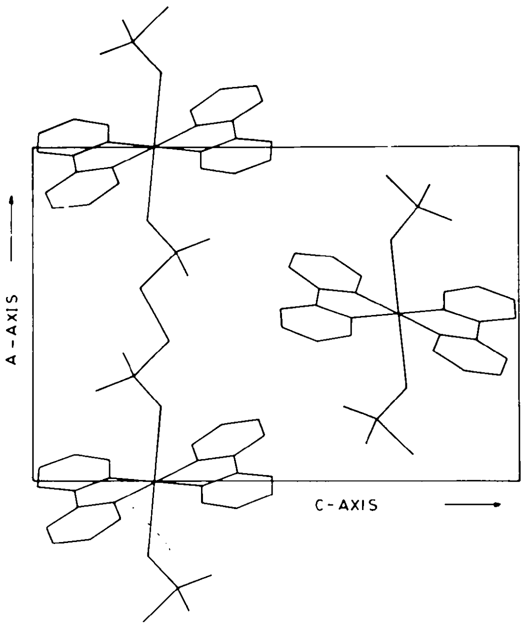

Fig. 2. The projection of the crystal structure of Cu(2,2′-bipyridyl)$_2$S$_4$O$_6$ along the *b* axis.

orientated at angle of 9·45° with respect to each other; there are no unusual bond lengths or angles in the 2,2′-bipyridyl ligands (Tables 2 and 3). Cubpy$_2$S$_4$O$_6$ is nearly isomorphous with the corresponding Cubpy$_2$S$_3$O$_6$ complex [a = 10·29 (2), b = 13·05 (2), c = 16·38 (2) Å, *Pbcn*, Cu–N = 1·98, Cu–O(2) = 2·82 Å; Ferrari, Fava & Pelizzi, 1977] crystallizing in the same space group and only differing significantly in the *a* axis length, reflecting the presence of an additional sulphur atom in the anion. Both complexes involve comparable stereochemistries for the CuN$_4$O$_2$ chromophores, but there is a significant difference in the Cu–O(1) bond lengths of 2·627 and 2·82 Å respectively, which yielded tetragonalities ($T = R_S/R_L$) of 0·76 and 0·71 respectively. This difference in the observed tetragonalities is surprising in view of the similarity of the electronic reflectance spectra which involve a single broad peak at 14 700 and 14 930 cm^{-1} for the trithionate and tetrathionate complexes respectively. It is of interest that the elongated rhombic octahedral chromophore is regular in both thionates, which contrasts with the irregular CuN$_4$O$_2$ chromophore in Cubpy$_2$(ClO$_4$)$_2$ (Nakai, 1971) with two clearly different out-of-plane Cu–O bonds of 2·45 and 2·73 Å respectively, despite the fact that the dihedral angles between the 2,2′-bipyridyl ligands are comparable (37°) and the corresponding O(1)–Cu–O(2) angles are similar (156·2°). The thionate structures also contrast with the stereochemistry in (Cubpy$_2$ONO$_2$)NO$_3$.H$_2$O (Nakai, Ooi & Kuroya, 1970) which involves a very distorted five-coordinate CuN$_4$O chromophore.

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Thallium(III) Triacetate

By R. Faggiani and I. D. Brown

Institute for Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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Abstract. Tl(O$_2$CCH$_3$)$_3$, monoclinic, $C2/c$, a = 15·540 (10), b = 8·630 (7), c = 7·848 (6) Å, β = 113·92 (5)°, Z = 4, D_x = 2·57 g cm^{-3}. The structure determined by X-ray diffraction (R_w = 0·057) shows that the Tl atom is chelated by the three acetate groups (Tl–O distances between 2·26 and 2·34 Å) and forms two further bonds (2·57 Å) to adjacent molecules along the *c* axis.

Introduction. Commercial thallium triacetate (Alfa Products) was recrystallized from acetic anhydride. A cylindrical crystal of radius 0·15 mm and length 0·25 mm, corresponding to [10$\bar{1}$], was mounted on a Syntex $P\bar{1}$ diffractometer. Lattice parameters were found from the settings of 15 well centered reflections with 20° ≤ 2θ ≤ 30° [λ(Mo $K\alpha$) = 0·71069 Å]. Systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) indicated space groups Cc and $C2/c$. The latter was confirmed by the refinement. Intensities of 1224 reflections with $2\theta < 56°$ were measured using Mo $K\alpha$ radiation and, after correction for absorption (cylindrical absorption with $\mu r = 2{\cdot}5$), were averaged to give 1117 non-equivalent reflections of which 360 had intensities less than three times the standard error based on counting statistics. The structure was solved from the Patterson function and was refined by full-matrix least squares using the locally written program *CUDLS*, where $\sum w(|F_o| - |F_c|)^2$ was minimized.

The final agreement index R_2 {$= [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$} was 0·057 ($R_1$ = 0·060). The weight, w, was $(\sigma^2 + 0{\cdot}025F_o^2)^{-1/2}$ where σ is the standard error based on counting statistics. Zero weights were assigned to 222 reflections for which $I = 0$, or for which $I < 3\sigma_I$ and $|F_c| < |F_o|$. An extinction correction given by $F^* = F[1 + (0{\cdot}32 \times 10^{-6})\beta(2\theta)F^2]^{1/2}$ (Larson, 1967) was applied. Atomic scattering factors corrected for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). The final positional parameters are given in Table 1.† The H atoms were not located, and the largest features in the final difference synthesis had a magnitude of 0·5 e Å^{-3} and were associated with the Tl atom. The average parameter shift/estimated standard error, in the final cycle, was 0·02.

Table 2. *Bond lengths* (Å) *and angles* (°) *in* $Tl(O_2CCH_3)_3$

Tl—O(1)	2·26 (1) × 2	Tl—O(2)′	2·57 (1) × 2
Tl—O(2)	2·31 (1) × 2	Tl—O(3)	2·34 (1) × 2
C(1)—O(1)	1·25 (2) × 2	C(4)—O(2)	1·26 (2)
C(1)—C(2)	1·58 (4)	C(4)—O(3)	1·24 (2)
		C(4)—C(3)	1·50 (3)
O(1)—C(1)—O(1)	121 (2)	O(2)—C(4)—O(3)	117 (2)
O(1)—C(1)—C(2)	120 (1)	O(2)—C(4)—C(3)	121 (2)
		O(3)—C(4)—C(3)	121 (1)
Possible C—H···O interactions			
C(2)—O(2)	3·38 (3)	C(3)—O(3)	3·40 (3)
C(3)—O(1)	3·29 (3)	C(3)—O(3)	3·59 (2)
C(3)—O(1)	3·47 (3)		

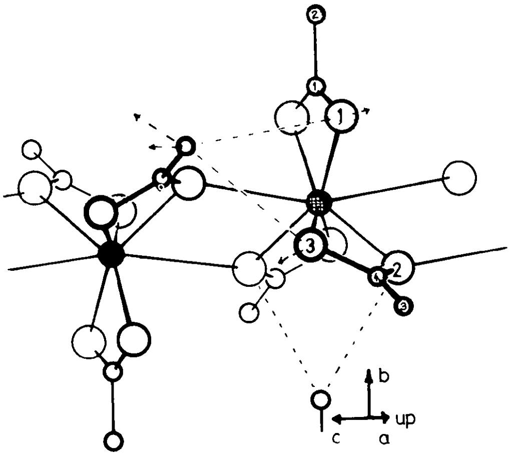

Fig. 1. Projection of two molecules of $Tl(O_2CCH_3)_3$ perpendicular to the bc plane showing intermolecular bonding along the c axis. Tl is shown cross hatched, O is shown with large circles, C with small circles. Some of the possible C—H···O interactions are shown with dashed lines.

Discussion. Selected interatomic distances and angles are given in Table 2, and a diagram of the structure is shown in Fig. 1. The Tl atom lies on a twofold axis and has an irregular eightfold coordination with the six shortest bonds to three chelating acetate groups. The remaining two Tl—O bonds link molecules into chains along the c axis. Chains are stacked in a pseudo-hexagonal array. A table of bond valences* shows that the experimentally determined atomic valences agree (within experimental error) with the theoretical values, confirming the correctness of the bond lengths (Brown & Shannon, 1973). Table 2 lists a number of C(methyl)—O distances in the range 3·2–3·6 Å that may represent very weak hydrogen-bonded interactions.

We wish to thank Dr A. McKillop for suggesting this problem and the National Research Council of Canada for an operating grant.

Table 1. *Fractional atomic coordinates* (×10^4)

	x	y	z
Tl	0	5633 (1)	2500
O(1)	707 (9)	7936 (16)	2538 (18)
O(2)	566 (7)	3846 (14)	1018 (15)
O(3)	1501 (9)	4509 (18)	3777 (20)
C(1)	0	8648 (27)	2500
C(2)	0	473 (42)	2500
C(3)	2125 (13)	2762 (28)	2195 (29)
C(4)	1361 (12)	3727 (20)	2358 (26)

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† Lists of anisotropic temperature factors and structure factors, and a table of bond valences have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33599 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

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