

- CHOW, Y. M. & BRITTON, D. (1975b). *Acta Cryst.* **B31**, 1934–1937.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
- COX, E. G., SHORTER, A. J. & WARDLAW, W. (1938). *J. Chem. Soc.* pp. 1886–1888.
- DAVIES, A. G., MILLEDGE, H. J., PUXLEY, D. C. & SMITH, P. J. (1970). *J. Chem. Soc. (A)*, pp. 2862–2866.
- FORDER, R. A. & SHELDRIK, G. M. (1970). *J. Organometal. Chem.* **22**, 611–617.
- FUJII, H. & KIMURA, M. (1971). *Bull. Chem. Soc. Japan*, **44**, 2643–2647.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–216. Birmingham: Kynoch Press.
- KONNERT, J., BRITTON, D. & CHOW, Y. M. (1972). *Acta Cryst.* **B28**, 180–187.
- KUROSAWA, H. & OKAWARA, R. (1970). *Organometal. Chem. Rev.* **A6**, 65–117.
- LEE, A. G. (1970). *Quart. Rev.* **24**, 310–329.
- LUTH, H. & TRUTER, M. R. (1970). *J. Chem. Soc. (A)*, pp. 1287–1293.
- MILBURN, G. H. W. & TRUTER, M. R. (1967). *J. Chem. Soc. (A)*, pp. 648–651.
- NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160–177.
- POWELL, H. M. & CROWFOOT, D. (1934). *Z. Kristallogr.* **87**, 370–378.
- RAMOS, V. B. (1972). Ph.D. thesis, pp. 108–117, Univ. of Minnesota.
- SCHLEMPER, E. O. & HAMILTON, W. C. (1966). *Inorg. Chem.* **5**, 995–998.
- SHIER, G. D. & DRAGO, R. S. (1966). *J. Organometal. Chem.* **5**, 330–340.
- TOBIAS, R. S. (1966). *Organometal. Chem. Rev.* **1**, 93–129.

Acta Cryst. (1975). **B31**, 1929

The Crystal Structures of Dimethylthallium Acetate, Tropolonate, Acetylacetonate, and Dibenzoylmethide

BY YEH MEI CHOW AND DOYLE BRITTON

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

(Received 26 September 1974; accepted 19 February 1975)

The crystal structures of dimethylthallium acetate, tropolonate, acetylacetonate, and dibenzoylmethide have been studied. The crystal data are as follows. $(\text{CH}_3)_2\text{Tl}(\text{OAc})$: $a = 7.43$, $b = 12.12$, $c = 7.79$ Å, $Imcm$, $Z = 4$. $(\text{CH}_3)_2\text{Tl}(\text{trop})$: $a = 7.89$, $b = 16.76$, $c = 7.88$ Å, $\beta = 100.3^\circ$, $I2/c$, $Z = 4$. $(\text{CH}_3)_2\text{Tl}(\text{acac})$: $a = 7.85$, $b = 14.52$, $c = 8.47$ Å, $Cmcm$, $Z = 4$. $(\text{CH}_3)_2\text{Tl}(\text{bzbz})$: $a = 14.18$, $b = 38.64$, $c = 17.33$ Å, $Pbca$, $Z = 24$. The structures of the acetate, tropolonate, and acetylacetonate have been determined and refined using three-dimensional counter data. Only a partial study of the dibenzoylmethide has been made. In each structure the anion forms a chelate ring with the thallium atom to give a neutral monomeric unit. In the acetate, tropolonate, and acetylacetonate, monomeric units are held together by further Tl–O bonds to form infinite linear polymers, with sixfold coordination around each thallium atom; this sixfold coordination is highly distorted from a regular octahedral arrangement in a way that varies regularly with the size of the chelate ring. In the dibenzoylmethide the monomeric units associate to form dimers with fivefold coordination around the thallium atoms; further polymerization is blocked by steric hindrance between phenyl groups.

Introduction

As part of a study of the coordination of the dimethylthallium group (Chow & Britton, 1975) we have studied the structures of four dimethylthallium chelate compounds.

A tetrahedral structure has been suggested for dimethylthallium β -diketonates because of the appreciable vapor pressure of the solids and their solubility in non-polar solvents (Menzies, Sidgwick, Cutcliffe & Fox, 1928). Cox, Shorter & Wardlaw (1938) made a preliminary X-ray crystallographic study of dimethylthallium acetylacetonate from which they tentatively drew the same conclusion. On the other hand, Kuro-

sawa, Yasada & Okawara (1965) have interpreted the infrared spectrum of this compound to indicate a linear dimethylthallium group, although in a later paper (1967) they suggest bent groups in similar compounds. The X-ray diffraction study of diethyl(salicylaldehydato)thallium(III) (Milburn & Truter, 1967) shows a polymeric structure with nearly linear C–Tl–C groups in the solid state although the compound is monomeric in chloroform solution.

In order to include a range of chelate ring sizes we have determined the structures of dimethylthallium acetate, $(\text{CH}_3)_2\text{Tl}(\text{OAc})$, dimethylthallium tropolonate, $(\text{CH}_3)_2\text{Tl}(\text{trop})$, and dimethylthallium acetylacetonate, $(\text{CH}_3)_2\text{Tl}(\text{acac})$. In addition, when a comparison of

these structures suggested that steric effects from non-bonded interactions might be important, we also began a study of the structure of dimethylthallium dibenzoylmethide, $(\text{CH}_3)_2\text{Tl}(\text{bzbz})$. This structure proved to be unusually complex and we only report here a partial study; however, we intend no further work on this compound.

Experimental

Preparations

Dimethylthallium acetate was prepared by refluxing dimethylthallium iodide and silver acetate in methanol. The crystals obtained from evaporation of the filtrate were recrystallized from a methanol-benzene mixture to obtain crystals suitable for the diffraction studies. Needle- and plate-like crystals were formed; both gave the same diffraction pattern. (Calculated: C, 16.37; H, 3.09%. Found: C, 16.40; H, 2.99%.)

Dimethylthallium tropolonate was prepared by the reaction of dimethylthallium hydroxide and tropolone

in methanol. Crystals suitable for the diffraction study were obtained by recrystallization from a methanol-benzene mixture. (Calculated: C, 30.33; H, 3.35%. Found: C, 30.28; H, 3.12%.)

Dimethylthallium acetylacetonate was prepared by the method of Menzies, Sidgwick, Cutcliffe & Fox (1928). Crystals suitable for diffraction studies were prepared by recrystallization from benzene.

Dimethylthallium dibenzoylmethide was prepared by the method of Shier & Drago (1966) and recrystallized from a benzene-hexane mixture. (Calculated: C, 44.61; H, 3.75%. Found: C, 44.54; H, 3.66%.)

Space groups and unit cells

All data were collected using Zr-filtered Mo $K\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$). The crystal data are summarized in Table 1. For the tropolonate ten planes and for the dibenzoylmethide 11 planes, each measured in four reflecting positions, were used for the least-squares calculation of the cell constants. In the other two cases, with small crystals and low intensities, the cell constants

Table 1. *Crystal data for $(\text{CH}_3)_2\text{Tl}(\text{chelate})$*

All measurements at room temperature, 18–22°C.

Chelate	OAc	trop	acac	acac*	bzbz
F.W.	293.48	356.39	333.55		457.70
<i>a</i> (Å)	7.43†	7.886 (5)	7.85	7.87	14.177 (11)
<i>b</i> (Å)	12.12	16.764 (17)	14.52	14.53	38.640 (13)
<i>c</i> (Å)	7.79	7.877 (4)	8.47	8.45	17.327 (8)
β (°)		100.30 (6)			
Space group	<i>Imcm</i>	<i>I2/c</i>	<i>Cmcm</i>	<i>C222₁</i>	<i>Pbca</i>
<i>Z</i>	4	4	4	4	24
Molecular volume (Å ³)	175.4	256.2	241.5		395.5
D_{obs} (g cm ⁻³)	2.7 (1)	2.30 (2)	2.24 (2)		1.96 (2)
D_{calc} (g cm ⁻³)	2.78	2.309	2.29		1.921

* Cox, Shorter & Wardlaw (1938). The orientation of their cell has been changed to agree with ours.

† Values in parentheses are e.s.d.'s from least-squares treatment of the diffractometer data. If e.s.d.'s are not given, the cell constants were measured from precession photographs and we estimate the accuracy to be no greater than 1 part in 500.

Table 2. *Intensity collection data for $(\text{CH}_3)_2\text{Tl}(\text{chelate})$*

	OAc	trop	acac	bzbz
Crystal size				
along <i>a</i> (mm)	0.28	0.10	*	0.30†
along <i>b</i> (mm)	0.064	0.16	0.12	0.18
along <i>c</i> (mm)	0.04	0.30	0.20	0.30
Spindle axis	<i>a</i>	<i>c</i>	<i>c</i>	<i>a</i>
Linear absorption coefficient (cm ⁻¹)	231	158	168	103
Minimum transmission coefficient	0.249	0.350	0.039	†
Maximum transmission coefficient	0.415	0.519	0.144	
Maximum θ (°)	24	25	26	16
Scan time per step (s)	6	4	4	2
Total background time/total scan time	0.5	0.5	0.5	1.0
Number of regular reflections between check reflections	40	50	50	30
Check reflection intensity: final/initial	0.98	0.96	0.89	0.96
Number of reflections measured	737	972	1259	2498
Number of independent reflections	366	901	548	2326
Number of independent reflections with $I > 2\sigma(I)$	270‡	778	383	1384

* Distance between $(\bar{1}10)$ and $(1\bar{1}0)$: 0.20 mm; between $(1\bar{1}0)$ and (110) : 0.16 mm.

† The crystal had an octahedral shape. These are distances along the octahedral axes. No absorption corrections were made for this crystal.

‡ For the acetate only, $I > \sigma(I)$.

were determined from precession photographs. The space groups were partially indicated by the systematic extinctions (OAc: $hkl, h+k+l=2n+1$ and $h0l, l=2n+1$; trop: $hkl, h+k+l=2n+1$ and $h0l, l=2n+1$; acac: $hkl, h+k=2n+1$ and $h0l, l=2n+1$; bzbz: $0kl, k=2n+1, h0l, l=2n+1, hk0, h=2n+1$) and were eventually determined by the complete solution of the structure, except for the dibenzoylmethide where the systematic extinctions alone give an unambiguous choice. The density was determined in each case by flotation in a chloroform–bromoform mixture.

Data collection

The acetate and tropolonate grew as parallelepipeds, the acetylacetonate as hexagonal prisms, and the dibenzoylmethide as octahedra. The crystal dimensions and mounting orientations are given in Table 2. The diffractometer geometry, data handling, and programs used were those described in the previous paper (Chow & Britton, 1975). Those details of the data collection that differed among the crystals are also given in Table 2.

Solution and refinement

The factors r and R , the scattering factors used, and the anomalous dispersion corrections were all the same as the previous paper. No attempt was made to include hydrogen atoms.

Dimethylthallium acetate

A trial structure in space group $Imcm$ was found from a Patterson map, improved from a Fourier map, and refined with anisotropic thermal parameters for the thallium atom and isotropic thermal parameters for the other atoms. The refinement converged with $r=0.012$, $R=0.059$. A difference Fourier map at this point showed no unusual features; the calculated F values for the weak reflections that had been omitted from the refinement were reasonable. Since the results at this point were acceptable on all points, we concluded that it was unnecessary to test for the possibility that the space group had lower symmetry than $Imcm$. The final parameters are given in Tables 3 and 4.*

Dimethylthallium tropolonate

A trial structure was found in space group $I2/c$ from Patterson and Fourier maps and refined with anisotropic thermal parameters for the thallium atom and isotropic thermal parameters for the remaining atoms. This refinement converged with $r=0.0085$, $R=0.046$. A difference Fourier map at this point showed no unusual features; the calculated structure factors for the weak reflections that had been omitted from the

refinement were all reasonable. Therefore, no further consideration was given to Ic as the possible space group. The final parameters are given in Tables 3 and 4; the observed and calculated structure factors are available.*

Dimethylthallium acetylacetonate

A trial structure in space group $Cmcm$ was found from the Patterson map, improved from a Fourier map, and refined with anisotropic thermal parameters for the thallium atom and isotropic thermal parameters for the remaining atoms. The refinement converged at $r=0.022$, $R=0.103$. The structure factors calculated for the reflections classified as unobserved had a reasonable distribution of low values. This plus the general consistency of the structure with the previous two led us to accept $Cmcm$ as the correct space group.

* See previous footnote.

Table 3. Positional and isotropic thermal parameters

Estimated standard deviations for the final significant figures are given in parentheses. The positional parameters that are not simple fractions are multiplied by 10^4 . The isotropic thermal parameters for the thallium atoms are calculated from the anisotropic thermal parameters (Table 4).

	x	y	z	B
Acetate				
Tl(a)	0	1713 (2)	$\frac{1}{4}$	4.2
O	1459 (31)	3668 (16)	$\frac{1}{4}$	6.2 (5)
C(1)	0	4193 (30)	$\frac{1}{4}$	3.5 (8)
C(2)	0	5354 (42)	$\frac{1}{4}$	7.0 (13)
C(3)	0	1592 (24)	5131 (51)	6.9 (8)
Tropolonate				
Tl(b)	0	-410 (1)	$\frac{3}{4}$	3.6
O	122 (11)	844 (6)	5870 (12)	4.8 (2)
C(1)	134 (15)	1502 (8)	6572 (16)	3.9 (2)
C(2)	424 (17)	2198 (8)	5648 (18)	4.6 (3)
C(3)	413 (19)	3001 (10)	6057 (20)	5.5 (3)
C(4)	0	3385 (13)	$\frac{3}{4}$	5.8 (5)
C(5)	2728 (23)	-555 (10)	7931 (25)	6.6 (4)
Acetylacetonate				
Tl(c)	0	-224 (1)	$\frac{3}{4}$	5.2
O	0	1076 (14)	5659 (27)	6.2 (5)
C(1)	0	1936 (22)	5971 (43)	5.6 (8)
C(2)	0	2311 (29)	$\frac{3}{4}$	5.0 (10)
C(3)	0	2538 (20)	4673 (35)	4.5 (7)
C(4)	2692 (62)	-352 (25)	$\frac{3}{4}$	9.0 (11)
Dibenzoylmethide				
Tl(1)	723	9829	960	
Tl(2)	1437	6475	713	
Tl(3)	459	3168	896	

Table 4. Anisotropic thermal parameters ($\times 10^4$) for Tl atoms

The Tl atoms can be identified by reference to Table 3. The anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$. β_{12} and β_{23} are 0 for all the atoms.

	β_{11}	β_{22}	β_{33}	β_{13}
Tl(a)	122 (3)	77 (2)	221 (4)	0
Tl(b)	185 (1)	38 (0)	95 (1)	44 (1)
Tl(c)	200 (5)	53 (1)	216 (4)	0

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30958 (27 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The final parameters are given in Tables 3 and 4; the observed and calculated structure factors are available.*

Dimethylthallium dibenzoylmethide

When the size and symmetry of the unit cell made it apparent that there were three monomer units in the asymmetric unit, it was decided that a complete determination of the structure of this compound was not economically reasonable. However, a partial study was made to determine the broad features of the stereochemistry. Data were collected only out to $\theta = 16^\circ$ and were not corrected for absorption. The thallium positions were determined from a Patterson map. Since they are approximately related by a translation of $a/3$, the thallium atoms were refined by least-squares calculations with anisotropic thermal parameters ($R = 0.22$) before a difference Fourier map was calculated. The thallium atoms occur in pairs about 4 Å apart. The center of one pair is on a center of symmetry; the other pair is composed of two crystallographically independent thallium atoms. The difference Fourier map does not show all of the carbon and oxygen atoms separately but the methyl carbon atoms show clearly, the chelate ring shows as a ring of electron density, and there are indications of the benzene rings. At this point our question was answered and refinement was terminated. The thallium positions are given in Table 3. It does not seem worthwhile to list the structure factors since they are only for low angles and are not corrected for absorption.

* See footnote on p. 1931.

Table 5. Distances (Å) and angles ($^\circ$)

	OAc	trop	acac	bzbz
Tl...Tl	4.178 (6)	4.171 (2)	4.284 (7)	4.13 4.11
O...O'	2.17 (5)	2.61 (2)	3.12 (5)	3.1 (av.)
Tl-O(chelate)	2.61 (2)	2.47 (1)	2.45 (2)	2.4 (av.)
Tl...O(bridge)	2.67 (2)	2.74 (1)	2.95 (2)	2.7 (av.)
Tl-CH ₃	2.05 (4)	2.13 (2)	2.12 (5)	2.1 (av.)
C-O	1.26 (3)	1.23 (2)	1.28 (4)	
C(1)-C(1')		1.51 (3)		
C(1)-C(2)	1.41 (6)	1.42 (2)	1.41 (4)	
C(1) or C(2)-C(3)		1.38 (2)	1.40 (5)	
C(3)-C(4)		1.39 (2)		
	OAc	trop	acac	
CH ₃ -Tl-CH ₃	171.8 (16)	166.9 (9)	170.0 (20)	
O-Tl-O	49.2 (10)	63.7 (4)	79.1 (11)	
O-Tl...O	75.4 (7)	73.8 (3)	75.3 (7)	
O...Tl...O	160.1 (8)	149.2 (4)	130.4 (8)	
Tl-O...Tl	104.6 (7)	106.2 (3)	104.7 (7)	
Tl-O-C(1)	95.8 (19)	121.7 (8)	128.5 (22)	
O-C(1)-[O, C(1'), C(2)]	119.2 (35)	116.2 (8)	124.8 (32)	
O-C(1)-[C(2), C(2), C(3)]	120.4 (26)	119.7 (12)	116.6 (30)	
C(1)-C(2)-C(1)			134.3 (41)	
C(1')-C(1)-C(2)		124.0 (8)		
C(1)-C(2)-C(3)		132.4 (13)		
C(2)-C(3)-C(4)		130.6 (15)		
C(3)-C(4)-C(3')		125.0 (20)		

Results and discussion

The structures of the acetate, the tropolonate, and the acetylacetonate are shown in Figs. 1, 2, and 3,

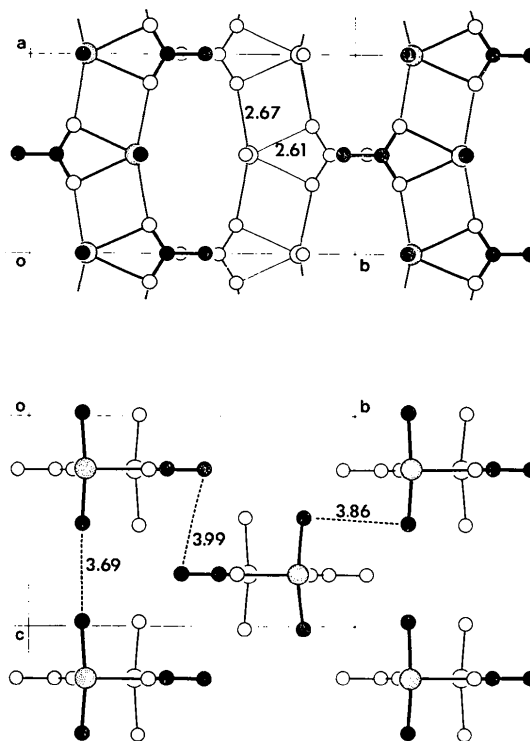


Fig. 1. The structure of dimethylthallium acetate. Top: view along *c*. Bottom: view along *a*. Distances are given in Å. Large atoms are thallium; small open atoms are oxygen; small solid atoms are carbon; hydrogens are omitted. All atoms in molecules that are to the rear in each view are left open.

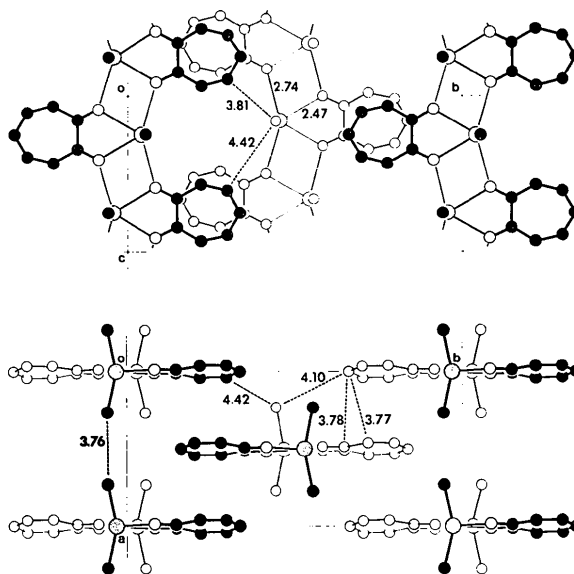


Fig. 2. The structure of dimethylthallium tropolonate. Top: view perpendicular to the (100) plane. Bottom: view along *c*. Distances are given in Å. Conventions are as in Fig. 1.

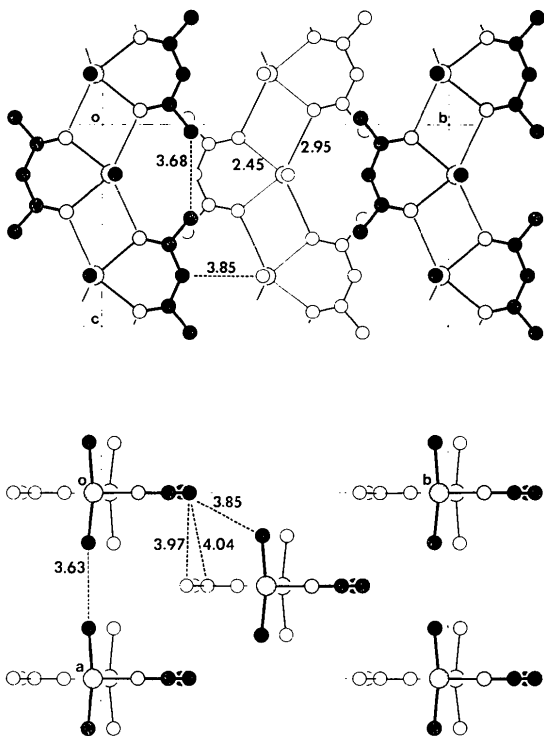


Fig. 3. The structure of dimethylthallium acetylacetonate. Top: view along *a*. Bottom: view along *c*. Distances are given in Å. Conventions are as in Fig. 1.

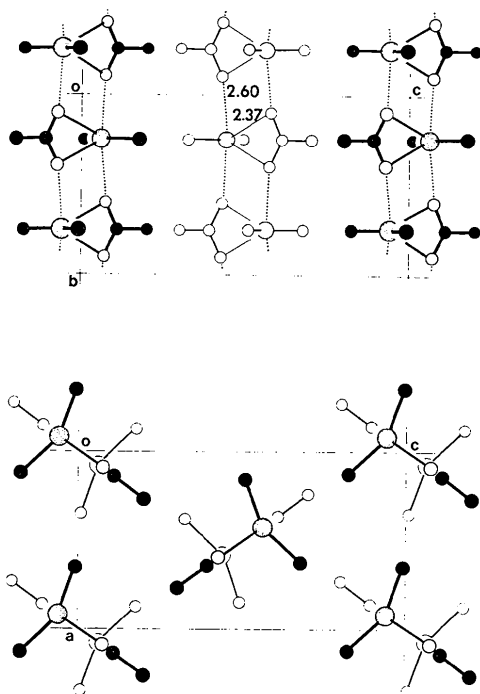


Fig. 4. The structure of dimethylindium acetate (Einstein, Gilbert & Tuck, 1973). Top: view along *a*. Bottom: view along *b*. Distances are given in Å. Conventions are as in Fig. 1.

respectively. Bond lengths and angles are given in Table 5. In each structure, as well as with the dibenzoylmethide (not shown), with diethyl(salicylaldehydato)-thallium(III) (Milburn & Truter, 1967), and with dimethyl-1,10-phenanthroline-thallium perchlorate (Blundell & Powell, 1972) the monomer unit can be described as a highly distorted tetrahedral arrangement. This is an artificial point of view since polymerization increases the coordination number to five in the dibenzoylmethide and to six in the others, but it does give a starting point for describing the geometry. This distorted tetrahedron has approximate or exact $mm2$ (C_{2v}) symmetry with a $\text{CH}_3\text{-Tl-CH}_3$ angle near 170° in every case and an O-Tl-O (or N-Tl-N) angle that varies with the size of the chelate ring. Although the angle in the chelate ring would not be expected to change much, the $\text{CH}_3\text{-Tl-CH}_3$ angle presumably could be closer to the tetrahedral angle in an isolated monomer. However, another artificial aspect of considering the isolated tetrahedral molecule is that the Tl-C bonds, which are all equal within experimental error to the value of $2.11(3)$ Å found in the preceding paper (Chow & Britton, 1975), appear to be covalent, and the Tl-O bonds considerably more ionic. In this respect the Tl^{III} is similar to Hg^{II} and, as with Hg^{II} compounds, the arrangement might better be described as linear, covalent $\text{CH}_3\text{-Tl-CH}_3$ groups distorted somewhat by weaker, ionic bonds around the equator.

In the acetate, tropolonate, and acetylacetonate the actual coordination number is six, the thallium atoms being coordinated to oxygen atoms in adjacent monomer units. The coordination polyhedra are topologically the usual octahedron although they are greatly distorted toward the unfamiliar second alternative (Britton & Dunitz, 1973). The distortion appears to be entirely a consequence of the chelate ring; the $\text{O}\cdots\text{O}$ distance in the chelate and the Tl-O distance determine the O-Tl-O bite angle, and the adjacent $\text{O-Tl}\cdots\text{O}$ angle is about 75° in all three compounds. If we use the very crude model that the Tl and O are hard spheres with ionic charges of $+1$ and $-\frac{1}{2}$, respectively, we can calculate an expected $\text{O-Tl}\cdots\text{O}$ angle of 64° in a four-membered Tl_2O_2 ring, to be compared with the observed 75° .

The association into infinite linear polymers is essentially the same in the acetate, tropolonate, and acetylacetonate. Also, in dimethylindium acetate (Einstein, Gilbert & Tuck, 1973) almost identical polymeric chains are found. In each of those four compounds each infinite chain is surrounded by six others aligned in a close-packed arrangement, as can be seen in the lower view in Figs. 1-4. However, as closer inspection of the figures will show, and the space group data in Table 1 will confirm, the details of the packing are different in the four structures. It is surprising that the relatively small changes in the dimensions within the chain on going from dimethylindium to dimethylthallium acetate should produce such a large change in the relative orientation of the chains, but the other

differences are more reasonable since the detailed shapes of the chains are considerably different. Some of the distances between non-bonded atoms are shown in Figs. 1–3. There are no unusually short distances between chains; the short (3.6–3.8 Å) $\text{CH}_3 \cdots \text{CH}_3$ distance along the vertical axis in the lower view in each figure is not short if $\text{C} \cdots \text{H}$ and $\text{H} \cdots \text{H}$ distance are considered rather than using an average radius for the methyl group. The one non-bonded distance that is slightly short is the 3.68 Å distance between CH_3 groups on adjacent acetylacetonate rings; this short distance plus the longer 2.95 Å $\text{Tl} \cdots \text{O}$ distances suggest that steric crowding might be beginning to be important in the geometry of the polymer. It was this observation that led us to look at the dibenzoylmethide where the ring methyl groups are replaced by phenyl groups.

As described in the *Experimental* section the structure of dimethylthallium dibenzoylmethide was not studied in detail. It was carried to the point where the thallium atoms were exactly located and the light atoms were approximately located. The thallium atoms occur in pairs about 4.1 Å apart, *i.e.* about the same distance apart as in the polymer chains in the other structures. This indicates that molecules occur as dimers rather than as infinite polymers. There are two independent dimer molecules in the unit cell. The light atom positions, except for the phenyl ring orientations, are about the same in both dimers, and are about the same as they are in a dimeric fragment of the acetylacetonate structure. It is clear from looking at the

latter structure (Fig. 3) that the replacement of methyls by phenyls should block polymerization beyond the dimer.

We wish to thank the National Science Foundation for its support of the research. The diffractometer was purchased under the Chemistry Research Instruments Program of the National Science Foundation in cooperation with the Graduate Research Center of the University of Minnesota.

References

- BLUNDELL, T. L. & POWELL, H. M. (1972). *Proc. Roy. Soc. A* **331**, 161–169.
 BRITTON, D. & DUNITZ, J. D. (1973). *Acta Cryst. A* **29**, 362–371.
 CHOW, Y. M. & BRITTON, D. (1975). *Acta Cryst. B* **31**, 1922–1929.
 COX, E. G., SHORTER, A. J. & WARDLAW, W. (1938). *J. Chem. Soc.* pp. 1886–1888.
 EINSTEIN, F. W. B., GILBERT, M. M. & TUCK, D. G. (1973). *J. Chem. Soc. Dalton*, pp. 248–251.
 KUROSAWA, H., YASUDA, K. & OKAWARA, R. (1965). *Inorg. Nucl. Chem. Lett.* **1**, 131–135.
 KUROSAWA, H., YASUDA, K. & OKAWARA, R. (1967). *Bull. Chem. Soc. Japan*, **40**, 861–864.
 MENZIES, R., SIDGWICK, N. V., CUTCLIFFE, E. F. & FOX, J. M. C. (1928). *J. Chem. Soc.* pp. 1288–1291.
 MILBURN, G. H. W. & TRUTER, M. R. (1967). *J. Chem. Soc. (A)*, pp. 648–651.
 SHIER, G. D. & DRAGO, R. S. (1966). *J. Organometal. Chem.* **5**, 330–340.

Acta Cryst. (1975). **B31**, 1934

The Crystal Structures of Dimethylthallium Tricyanomethide and Dimethylthallium Dicyanamide

BY YEH MEI CHOW AND DOYLE BRITTON

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

(Received 26 September 1974; accepted 19 February 1975)

Dimethylthallium tricyanomethide, $(\text{CH}_3)_2\text{TlC}(\text{CN})_3$, is orthorhombic with $a = 26.123$ (9), $b = 6.264$ (3), $c = 21.007$ (7) Å, $Z = 16$, space group *Fddd*. Dimethylthallium dicyanamide, $(\text{CH}_3)_2\text{TlN}(\text{CN})_2$, is monoclinic with $a = 6.739$ (3), $b = 11.830$ (7), $c = 9.891$ (7) Å, $\beta = 117.81$ (3)°, $Z = 4$, space group *P2₁/c*. Least-squares refinement of diffractometer data converged at conventional *R* values of 0.047 and 0.081 respectively for the two compounds. In both crystalline compounds the thallium is octahedrally coordinated to the methyl groups and four nitrogen atoms. In the tricyanomethide two nitrogen atoms each bond to a single thallium atom at a distance of 2.67 Å, the third bonds equally to two thallium atoms at 2.91 Å. In the dicyanamide one terminal nitrogen atom and the central nitrogen atom each bond to a single thallium atom at distances of 2.60 and 2.90 Å, respectively; the other terminal nitrogen atom bonds to two thallium atoms at distances of 2.79 and 2.81 Å. The dimethylthallium groups are close to linear in both compounds.

Introduction

As part of a study of the coordination of the dimethylthallium group (Chow & Britton, 1975*a, b*) we report

here the structures of dimethylthallium tricyanomethide, $(\text{CH}_3)_2\text{TlC}(\text{CN})_3$, and dimethylthallium dicyanamide, $(\text{CH}_3)_2\text{TlN}(\text{CN})_2$. The particular reason for studying the tricyanomethide was to see whether the