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) $CH_3\cdots CH_3$ distance along the vertical axis in the lower view in each figure is not short if $C\cdots H$ and $H\cdots H$ 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 $Tl\cdots O$ 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.

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The Crystal Structures of Dimethylthallium Tricyanomethide and Dimethylthallium Dicyanamide

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Dimethylthallium tricyanomethide, $(CH_3)_2TlC(CN)_3$, is orthorhombic with $a = 26\cdot123$ (9), $b = 6\cdot264$ (3), $c = 21\cdot007$ (7) Å, $Z = 16$, space group *Fddd*. Dimethylthallium dicyanamide, $(CH_3)_2TlN(CN)_2$, is monoclinic with $a = 6\cdot739$ (3), $b = 11\cdot830$ (7), $c = 9\cdot891$ (7) Å, $\beta = 117\cdot81$ (3)°, $Z = 4$, space group $P2_1/c$. 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, $(CH_3)_2TlC(CN)_3$, and dimethylthallium dicyanamide, $(CH_3)_2TlN(CN)_2$. The particular reason for studying the tricyanomethide was to see whether the

C(CN)₃ group might lead to five-coordinate thallium in the same way that it leads to three-coordinate silver in $AgC(CN)_3$ (Konnert & Britton, 1966). With the dicyanamide, in addition to the interest in the coordination about the dimethylthallium group, we were interested in the manner in which the dicyanamide group coordinates to the metal, since in the structures of $(CH_3)_3SnN(CN)_2$ and $(CH_3)_2Sn[N(CN)_2]_2$ (Chow, 1971) we had found that only two of the three likely basis sites in the $N(CN)_2$ group had been coordinated to the metal atoms.

Experimental

Dimethylthallium tricyanomethide, $(CH_3)_2TlC(CN)_3$, F.W. 324·51, was prepared by refluxing $(CH_3)_2TlI$ with $AgC(CN)_3$ in methanol. The powder obtained by evaporation of the filtrate from the refluxing mixture was recrystallized from a methanol–benzene solution to give crystals suitable for X-ray diffraction studies.
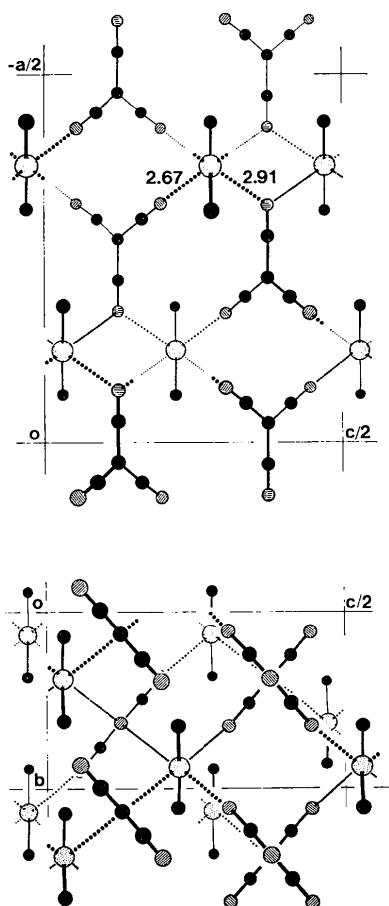

Fig. 1. The structure of dimethylthallium tricyanomethide. Top: view along **b**. Bottom: view along **a**. The N···Tl distances are given in Å. The large atoms are thallium; the small shaded atoms are nitrogen; the small solid atoms are carbon; hydrogen atoms are omitted.

(Calculated: C, 22·21; H, 1·86; N, 12·95%. Found: C, 22·46; H, 1·82; N, 13·08%.)

Dimethylthallium dicyanamide, $(CH_3)_2TlN(CN)_2$, F.W. 300·48, was prepared by refluxing $(CH_3)_2TlI$ with $AgN(CN)_2$ in methanol. The powder obtained from the slow evaporation of the filtrate was recrystallized from a mixture of methanol and benzene, which produced crystals suitable for X-ray diffraction studies. (Calculated: C, 15·99; H, 2·01; N, 13·98%. Found: C, 16·04; H, 1·94; N, 14·06%.)

The space groups were determined using precession photographs and the cell constants and intensity data were measured on a Hilger and Watts four-circle automated diffractometer using Mo $K\alpha$ radiation ($\lambda = 0·7107$ Å). For both compounds the cell constants were obtained from the diffractometer measurements of the Bragg angles of 12 planes, each of which was measured in four reflecting positions; the errors are e.s.d.'s from the least-squares refinement of the data.

For the tricyanomethide the crystals are orthorhombic with cell constants $a = 26·123(9)$, $b = 6·264(3)$, $c = 21·007(7)$ Å. The observed systematic requirements for reflection (hkl, all even or all odd; $hk0$, $h+k=4n$; $h0l$, $h+l=4n$; $0kl$, $k+l=4n$) indicate the space group to be $Fddd$ (D_{2h}^{24}). The calculated density of 2·507 g cm⁻³ for $Z = 16$ agrees reasonably well with the experimental value of 2·47(2) g cm⁻³ measured by flotation in a bromoform–chloroform mixture; the molecular volume is 214·8 Å³. In this space group $Z = 16$ requires that the $(CH_3)_2Tl$ groups and the $C(CN)_3$ groups each lie at least on a twofold special position.

The dicyanamide crystals are monoclinic with cell constants $a = 6·739(3)$, $b = 11·830(7)$, $c = 9·891(4)$ Å, $\beta = 117·81(3)°$. Systematic extinctions ($0k0$, $k=2n+1$; $h0l$, $l=2n+1$) indicate the space group to be $P2_1/c$ (C_{2h}^5). For four molecules per unit cell the molecular volume is 174·4 Å³, which is reasonable when compared with the molecular volumes of the dimethylthallium pseudohalides; the calculated density of 2·861 g cm⁻³ agrees with the experimental value of 2·83(2) g cm⁻³ measured by flotation in a bromoform–chloroform mixture.

The crystal of the tricyanomethide used for intensity measurements was a tabular prism mounted with the b axis parallel to the φ axis of the diffractometer. It was bounded by the two planes of the {100} form each 0·05 mm from the crystal center, the four planes of the {011} form each 0·10 mm from the crystal center, and the two planes of the {001} form each 0·09 mm from the crystal center. The absorption coefficient for Mo $K\alpha$ radiation is 189 cm⁻¹.

The crystal of the dicyanamide used for intensity measurements was a needle elongated along the [101] direction and showing $2/m$ symmetry. It was mounted with the needle axis parallel to the φ axis of the diffractometer. It was bounded on the sides by the four planes of the form {12$\bar{2}$} at a distance of 0·028 mm from the center of the crystal and terminated by the eight planes of the {011} and {11$\bar{1}$} forms all at a

distance of 0·012 mm from the center of the crystal. The absorption coefficient for Mo $K\alpha$ radiation is 232 cm^{-1}.

The diffraction geometry and scanning arrangement were those described in the first paper of this series (Chow & Britton, 1975a). In the following discussion the variable appropriate to the tricyanomethide will be given first, then the corresponding variable for the dicyanamide (in parentheses) if it is different. Data were collected over one quadrant (hemisphere) out to $\theta = 24°$ (22°). Scans of 100 0·01° steps of 3s each were used with a total background counting time of 150. The data were monitored by checking two test reflections every 40 regular reflections. The test reflections decreased 5% (23%) in intensity over the course of the data collection. The intensities of the regular reflections were corrected for the decrease by linear interpolation. In total, 1721 (2006) reflections were measured, of which 672 (859) were independent. The equivalent reflections were combined and only the 417 (686) independent reflections for which $I > 2\sigma(I)$ were used in the subsequent calculations. Lorentz and polarization corrections were made; absorption corrections were made by a point-by-point integration. All calculations were made as described in Chow & Britton (1975a). The same atomic scattering factors, anomalous dispersion corrections, and computer programs were used.

Solution and refinement

The structures were solved from Patterson and Fourier maps and refined by least-squares calculations using anisotropic thermal parameters for the thallium atoms and isotropic thermal parameters for the light atoms. Hydrogen atoms were not considered. Refinement converged with $r = 0·011$ and $R = 0·047$ for the tricyanomethide, and $r = 0·037$ and $R = 0·081$ for the dicyanamide.* The final parameters are given in Table 1.

Results and discussion

The structures are shown in Figs. 1 and 2. Bond lengths and angles are given in Table 2.

In the $(CH_3)_2TlC(CN)_3$ structure the bond lengths and angles in the dimethylthallium ion and in the tricyanomethide ion are normal within experimental error. The envisaged five-coordination around the thallium atom does not occur. Rather, two of the nitrogen atoms in the anion coordinate to single thallium atoms and the third coordinates to two so that the coordination around the thallium is sixfold and, notwith-

standing the differences in the Tl–CH_3 and Tl–N distances, is only slightly distorted from the directions in a regular octahedral arrangement. Although we would describe the Tl–N bonds as ionic, it is worth noting that the two Tl–N bonds and the two remaining cyanide groups are disposed in an allene-like fashion about the C–C–N atoms that lie on the twofold axis.

Table 1. *Positional and 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 anisotropic thermal parameters by 10^5. The anisotropic thermal parameters are of the form exp $[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

	x	y	z	B
$(CH_3)_2TlC(CN)_3$				
Tl(A)	$\frac{3}{8}$	$-\frac{1}{8}$	2210 (1)	3·89 (3)
N(1)	4281 (12)	$\frac{1}{8}$	$\frac{1}{8}$	5·3 (6)
N(2)	5741 (11)	-1431 (57)	566 (12)	8·6 (7)
C(1)	4715 (12)	$\frac{1}{8}$	$\frac{1}{8}$	3·9 (6)
C(2)	5522 (11)	-107 (47)	888 (13)	6·1 (6)
C(3)	5259 (11)	$\frac{1}{8}$	$\frac{1}{8}$	3·7 (6)
CH_3	3155 (10)	1078 (51)	2198 (10)	5·5 (5)
$(CH_3)_2TlN(CN)_2$				
Tl(B)	739 (2)	2653 (1)	4101 (1)	2·79 (6)
N(1)	3778 (61)	3825 (34)	735 (43)	5·0 (8)
N(2)	8793 (59)	6425 (29)	3166 (39)	4·3 (7)
N(3)	7613 (55)	4471 (23)	2566 (37)	3·4 (5)
C(1)	5613 (58)	4167 (34)	1532 (40)	3·6 (7)
C(2)	8085 (49)	5499 (24)	2867 (36)	2·1 (5)
CH_3(1)	3195 (64)	3757 (33)	4171 (44)	3·7 (7)
CH_3(2)	-1954 (68)	1572 (35)	3886 (48)	4·1 (8)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl(A)	141 (2)	2242 (36)	244 (3)	-89 (15)		
Tl(B)	2166 (51)	289 (12)	1020 (24)	-59 (15)	471 (25)	-12 (11)

Table 2. *Distances* (Å) *and angles* (°)

$(CH_3)_2TlC(CN)_3$

Tl——CH_3	2·13 (3)	CH_3–Tl——CH_3	178·7 (12)
Tl——N(1)	2·91 (1)	N(1)–Tl——N(1)	92·1 (6)
Tl——N(2)	2·67 (3)	N(2)–Tl——N(2)	95·2 (12)
		N(1)–Tl——N(2)	86·4 (7)
C(1)–C(3)	1·42 (4)	C(1)–C(3)–C(2)	121·0 (16)
C(2)–C(3)	1·33 (3)	C(2)–C(3)–C(2)	118·0 (31)
C(1)–N(1)	1·13 (4)	C(3)–C(1)–N(1)	180
C(2)–N(2)	1·21 (4)	C(3)–C(2)–N(2)	176·4 (31)
		C(1)–N(1)–Tl	118·5 (5)
		C(2)–N(2)–Tl	169·5 (25)

$(CH_3)_2TlN(CN)_2$

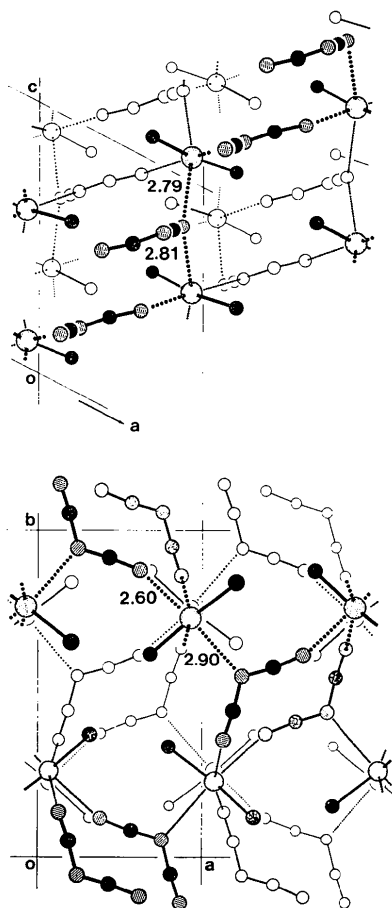| Tl——CH_3(1)	2·08 (4)	CH_3—Tl——CH_3	176·0 (13)
Tl——CH_3(2)	2·15 (5)	N(1)–Tl——N(2)	87·7 (12)
Tl——N(1)	2·60 (4)	N(1)–Tl——N(2')	78·4 (11)
Tl——N(2)	2·79 (4)	N(2)–Tl——N(3)	86·8 (10)
Tl——N(2')	2·81 (4)	N(2')–Tl——N(3)	106·9 (10)
Tl——N(3)	2·90 (3)	C(1)–N(3)–C(2)	120·4 (30)
N(3)–C(1)	1·31 (5)	C(1)–N(1)–Tl	156·5 (31)
N(3)–C(2)	1·26 (4)	C(1)–N(3)–Tl	116·0 (23)
C(1)–N(1)	1·19 (5)	C(2)–N(3)–Tl	123·5 (20)
C(2)–N(2)	1·18 (4)	C(2)–N(2)–Tl	117·2 (33)
N(3)–C(1)–N(1)	172·0 (44)	C(2)- N(2)–Tl'	117·6 (30)
N(3)–C(2)–N(2)	171·4 (43)	Tl——N(2)–Tl'	124·5 (12)

Fig. 2. The structure of dimethylthallium dicyanamide. Top: view along b. Bottom: view along c. The N···Tl distances are given in Å. Conventions are as in Fig. 1 except that atoms toward the rear of each view are not shaded.

In the $(CH_3)_2TlN(CN)_2$ structure the geometry of the dimethylthallium group is normal with the possible exception of being slightly bent. The geometry of the

anion is also the same within experimental error as in the only previous structures with this anion, $(CH_3)_3SnN(CN)_2$ and $(CH_3)_2Sn[N(CN)_2]_2$ (Chow, 1971), although the C–N–C angle here, 120(3)°, might be smaller than the previously observed 124(1) and 130(1)°. The environment of the anion here is distinctly different in that instead of the anion as a whole being bonded to two metal atoms as in the structures of both of the tin compounds, it is bonded to four. One terminal nitrogen atom and the central nitrogen atom are each bonded to a single thallium atom at 2·60 and 2·90 Å, respectively, while the other terminal nitrogen atom is bonded to two thallium atoms at distances of 2·79 and 2·81 Å. As was the case with the dimethylthallium tricyanomethide, while the cyanide group that forms a single bond to a thallium atom forms a nearly linear bond, C–N–Tl = 157°, the cyanide group that bonds to two thallium atoms is part of an N–C–N group that has an allene-like arrangement of another cyanide and a thallium atom bonded at one end and two thallium atoms bonded at the other. The coordination around the thallium atom is slightly distorted from a regular octahedral arrangement, the largest deviation from 90° being the 78 and 107° N–Tl–N angles. As with the majority of the structures studied in this series, the coordination might better be described as a linear, covalent CH_3–Tl–CH_3 group surrounded on the equator by four more ionic groups.

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