

The Crystal Structures of Dimethylthallium Cyanide, Azide, Cyanate, and Thiocyanate

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The crystal structures of dimethylthallium cyanide, azide, thiocyanate, and cyanate have been studied. The latter two compounds both exist in two polymorphic forms. The crystal data are as follows: $(\text{CH}_3)_2\text{TlCN}$: orthorhombic, $a=4.48$, $b=4.59$, $c=13.71$ Å, $Immm$, $Z=2$. $(\text{CH}_3)_2\text{TlN}_3$: monoclinic, $a=5.37$, $b=4.16$, $c=12.74$ Å, $\beta=100.7^\circ$, $I2/m$, $Z=2$. $(\text{CH}_3)_2\text{TlNCS}$: monoclinic, $a=14.04$, $b=4.32$, $c=14.62$ Å, $\beta=93.2^\circ$, $C2/m$, $Z=4$. $(\text{CH}_3)_2\text{TlNCS}$: orthorhombic, $a=10.51$, $b=4.34$, $c=14.56$ Å, $Pcma$, $Z=4$. $(\text{CH}_3)_2\text{TlNCO}$: orthorhombic, $a=11.09$, $b=4.09$, $c=12.81$ Å, $Pcma$, $Z=4$. $(\text{CH}_3)_2\text{TlNCO}$: trigonal, $a=18.28$, $c=9.47$ Å, $R\bar{3}m$, $Z=18$. The structures of the cyanide, azide, and monoclinic thiocyanate have a distorted sodium chloride structure similar to those of the dimethylthallium halides. The orthorhombic thiocyanate and cyanate differ from the previous three in that the infinite layers of composition $(\text{CH}_3)_2\text{TlX}$, which are similar in all five structures, pack together in a different way. The trigonal cyanate has a quite different structure with recognizable $[(\text{CH}_3)_2\text{TlNCO}]_2$ groups, which are held together through O-Tl bonds to form a three-dimensional polymer. The two polymorphic forms of the thiocyanate are also different chemically: in the monoclinic form alternate thallium atoms have four nitrogen atoms and four sulfur atoms as ligands, whereas in the orthorhombic form all thallium atoms have two nitrogen atoms and two sulfur atoms as ligands.

Introduction

In dimethyltin(IV) compounds, $(\text{CH}_3)_2\text{SnX}_2$, the tetrahedral arrangement that would be expected for an isolated molecule can be distorted in the solid, if the groups X still have some base capacity left, toward an octahedral arrangement. There are a number of compounds in which this octahedral arrangement can best be described as involving *trans* methyl groups, but with a wide range of $\text{CH}_3\text{-Sn-CH}_3$ angles. Gaseous $(\text{CH}_3)_2\text{SnCl}_2$ has regular tetrahedral bond angles within experimental error (Fujii & Kimura, 1971); in the solid (Davies, Milledge, Puxley & Smith, 1970) the $\text{CH}_3\text{-Sn-CH}_3$ angle is 123.5° ; that is, the distortion toward octahedral coordination is slight (but real). In $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ (Forder & Sheldrick, 1970; Chow, 1970) and in $(\text{CH}_3)_2\text{Sn}(\text{CN})_2$ (Konert, Britton & Chow, 1972) this angle is near 150° ; in $(\text{CH}_3)_2\text{SnF}_2$ (Schlemper & Hamilton, 1966), $(\text{CH}_3)_2\text{Sn}[\text{N}(\text{CN})_2]$ (Chow, 1971), and $(\text{CH}_3)_2\text{Sn}(\text{SO}_3\text{F})_2$ (Allen, Lerbscher, & Trotter, 1971) the change is complete and the angle is 180° . In this and the following two papers (Chow & Britton, 1975*a,b*) we examine the extent to which a similar phenomenon occurs in the $\text{CH}_3\text{-Tl-CH}_3$ group.

The known structures of dimethylthallium(III) compounds all show more or less octahedral coordination around the thallium. In $(\text{CH}_3)_2\text{TlX}$, X=Cl, Br, I (Powell & Crowfoot, 1934), the $\text{CH}_3\text{-Tl-CH}_3$ angle is 180° with $4/m\bar{m}$ symmetry at the thallium atom if the methyl hydrogen atoms are ignored; in dimethyl-1,10-phenanthroline-thallium perchlorate (Blundell & Powell, 1972) this angle is 168° although the coordination as a whole is greatly distorted from octahedral; indeed the authors say it cannot be de-

scribed as octahedral. In two other related structures, diethyl(salicylaldehydato)thallium(III) (Milburn & Truter, 1967) and hydroxobis(pentafluorophenyl)thallium(III) (Luth & Truter, 1970), the C-Tl-C angles are 172 and 139° , respectively, although in the latter compound there is only fivefold coordination. Cox, Shorter & Wardlaw (1938) began a crystallographic study of $(\text{CH}_3)_2\text{Tl}(\text{acac})$ and concluded that the coordination was either tetrahedral or planar, but they did not consider the possibility of polymerization in the solid. Discussions of the possible coordination around the thallium atom in dimethylthallium compounds and the conclusions to be drawn about the coordination from the observed infrared and Raman spectra have been discussed in several review articles (Tobias, 1966; Lee, 1970; Kurosawa & Okawara, 1970); the general conclusion is that the dimethylthallium group will generally be closer to linear than the dimethyltin group, but bent groups are possible and in some cases indicated.

In this paper we report the structures of some dimethylthallium pseudohalides; the cyanide, the azide, two polymorphic forms of the thiocyanate, and two polymorphic forms of the cyanate.

Experimental

Preparations

The starting material for all the preparations was dimethylthallium iodide, which was prepared by the method of Shier & Drago (1966), and recrystallized from ammonia solution.

Dimethylthallium cyanide was prepared by adding an equivalent amount of potassium cyanide to a

dimethylthallium nitrate solution. The nitrate had been prepared by refluxing silver nitrate and dimethylthallium iodide in methanol. It was not possible to prepare crystals suitable for single-crystal X-ray diffraction either by sublimation or by recrystallization from methanol, ethanol, or water, so that only powdered material was available for use. (Calculated: C, 13.83; H, 2.32; N, 5.38%. Found: C, 13.84; H, 2.40; N, 5.14%.)

Dimethylthallium azide was prepared by refluxing the iodide with silver azide in methanol. Sword-shaped crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate. (Calculated: C, 8.69; H, 2.19; N, 15.20%. Found: C, 8.49; H, 2.10; N, 15.03%.)

Dimethylthallium thiocyanate was prepared by refluxing the iodide with freshly prepared silver thiocyanate in methanol. Slow evaporation of the filtrate produced needle-like crystals (of the monoclinic form, see below) suitable for X-ray diffraction. (Calculated: C, 12.32; H, 2.07; N, 4.79; S, 10.96%. Found: C, 12.41; H, 2.10; N, 4.61; S, 10.79%.) On long standing the needle-like crystals became slightly brownish; recrystallization from a mixture of methanol and benzene produced sword-shaped crystals (of the orthorhombic form) also suitable for X-ray diffraction.

Dimethylthallium cyanate was prepared by refluxing the iodide with freshly prepared silver cyanate in acetonitrile. If the refluxing was continued 2–3 h, slow evaporation of the filtrate led to sword-like crystals (of the orthorhombic form, see below). (Calculated: C, 13.03; H, 2.19; N, 5.06%. Found: C, 12.95; H, 1.95; N, 4.81%.) When the refluxing was continued for 10–12 h, slow evaporation of the filtrate led first to large well-formed prismatic crystals (of the trigonal form) in the center of the evaporating dish and eventually to sword-like crystals (of the orthorhombic form) along the walls of the dish. The two forms could be separated mechanically. (Trigonal: calculated: C, 13.03; H, 2.19; N, 5.06%. Found: C, 13.25; H, 2.34; N, 5.04%.)

Space groups and unit cells

All data were collected with Zr-filtered Mo $K\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$) except for the powder data on $(\text{CH}_3)_2\text{TlCN}$, which were collected with V-filtered Cr $K\alpha$ radiation ($\lambda=2.2909 \text{ \AA}$). The crystal data are summarized in Table 1. The powder data for the cyanide were indexed by comparison with the calculated powder patterns for the chloride, bromide, and iodide (Powell & Crowfoot, 1934) and cell constants determined by analytical extrapolation of the Nelson & Riley (1945) function.* The cell constants of the monoclinic thiocyanate and the trigonal cyanate are from least-squares fits of the Bragg angles determined on the diffractometer. For both the thiocyanate and the cyanate eight planes, each measured in four reflecting positions, were used for the least-squares calculations; e.s.d.'s were determined as part of the calculation. In the other three cases, with small crystals and low intensities, the cell constants were determined from precession photographs. The space groups of the single crystals were determined from precession photographs by the observed systematic requirements for reflection (azide: $hkl, h+k+l=2n$; monoclinic thiocyanate: $hkl, h+k=2n$; in addition there is a pseudo condition for strong reflection: hkl , all even or all odd; orthorhombic thiocyanate and orthorhombic cyanate: $hk0, h=2n; 0kl, l=2n$; trigonal cyanate: $hkl, -h+k+l=3n$). In none of these cases is the choice of space group unique; the space groups given in Table 1 are those corresponding to the eventual complete solutions of the structure.

The numbers of molecules per unit cell were determined by comparison with the known structures of the dimethylthallium halides. As a check after the

* These powder data are available from the authors and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30956 (34 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

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

X System	CN		NCS		NCO		
	Orthorhombic	Monoclinic	Pseudo-cell	True cell	Orthorhombic	Orthorhombic Trigonal	
F.W.	260.46	276.46		292.52		276.46	
a (Å)	4.483 (3)	5.37	5.665 (3)	14.036 (11)	10.51	11.09	18.281 (7)
b (Å)	4.587 (4)	4.16	4.317 (3)	4.317 (3)	4.34	4.09	
c (Å)	13.706 (10)	12.74	13.044 (17)	14.617 (10)	14.56	12.81	9.474 (4)
β (°)		100.7	93.18 (7)	133.12 (4)			
Space group	$Immm$	$I2/m$	Im	$C2/m$	$Pcma$	$Pcma$	$R\bar{3}m$
Z	2	2	2	4	4	4	18
Molecular volume (Å ³)	140.9	139.9		161.6	165.9	145.4	152.3
D_{obs} (g cm ⁻³)		3.07 (2)		3.01 (2)			2.99 (2)
D_{calc} (g cm ⁻³)	3.069	3.28		3.005	2.93	3.16	3.015

structures were solved the densities of several of the compounds were determined by flotation in methylene iodide-bromoform mixtures. For the two structures for which there was any question about the solution, the monoclinic thiocyanate and the trigonal cyanate, the agreement between observed and calculated densities is satisfactory; for the azide the two densities do not agree. The azide crystals used for the density measurement appeared to be in good condition but were over two years old and were perhaps partly decomposed.

Data collection

Except for the trigonal cyanate, all of the crystals grew as flat needles with the long axis parallel to **b** and were oriented with **b** parallel to the φ axis of the diffractometer (for the monoclinic thiocyanate this was the *b* axis of the pseudocell). If the termination of the needle did not appear to be perpendicular to **b**, the crystal was cut so that it was. The dimensions of the crystals used are given in Table 2. The crystals of the trigonal cyanate were thick prisms bounded by the following planes at the indicated distances (in mm) from an arbitrary origin in the crystal: ($1\bar{2}0$) and ($\bar{1}20$)—0.060, ($2\bar{1}0$)—0.116, (101) and ($\bar{1}0\bar{1}$)—0.080, ($01\bar{1}$)—0.140, (021) and ($0\bar{2}\bar{1}$)—0.052, ($2\bar{2}1$) and ($\bar{2}2\bar{1}$)—0.080, ($20\bar{1}$) and ($\bar{2}01$)—0.160; the crystal was mounted with the [112] direction parallel to the φ axis of the diffractometer.

All intensity data were collected on a Hilger and Watts four-circle automated diffractometer. The same diffractometer geometry was used for all the crystals; the distance from the source of the crystal was 28 cm, from the crystal to the aperture 20 cm; a 6.0 mm diameter circular aperture was used; the take-off angle was 3°. A moving-crystal moving-detector scan was

used with 100 0.01° steps in θ and ω (120 steps for the two thiocyanate crystals), centered on the calculated setting. Background counts of 0.25 times the integrated scan time (0.50 times for the azide only) were taken at each end of the scan. Two test reflections were checked at periodic intervals to monitor any changes in the crystal or in the settings. The range in θ scanned, the frequency of the test reflections, and other details that varied from crystal to crystal are listed in Table 2.

All of the crystals except the orthorhombic thiocyanate partially decomposed in the X-ray beam, as shown by a steady decrease in the intensities of the test reflections. The measured intensities were corrected for this decomposition by being rescaled according to the intensities of the test reflections. The data were processed in the manner described by Corfield, Døedens & Ibers (1967); the value of 0.04 was used for p in the $\sigma(I)$ equation. Absorption corrections as well as the usual Lorentz and polarization corrections were made.* Intensities and $\sigma(I)$'s of equivalent reflections were averaged to give the numbers of reflections listed in Table 2 as independent reflections. Those independent reflections for which $I \leq 2\sigma(I)$ were omitted from further consideration.

* The computer programs used were: *POWDER*, a local program to calculate cell constants from Bragg angles; a local version of *PTC* (original program by B. G. Duerr) for initial processing of the diffractometer output; a local version of *DATAP2* (Coppens, Leiserowitz & Rabinovich, 1965) for Lorentz, polarization, and absorption corrections; *UMPREL* (by L. W. Finger) for Patterson maps; *UMLSTSQ* (by L. W. Finger) for Fourier maps and least-squares calculations; *BADTEA* (by L. W. Finger) for distances, angles, and errors. All calculations were made on the Control Data 6600 computer of the University Computer Center of the University of Minnesota.

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

	N ₃ Monoclinic	NCS Monoclinic	NCS Orthorhombic	NCO Orthorhombic	NCO Trigonal
Crystal size					
along a (mm)	0.22	0.08*	0.08	0.16	†
along b (mm)	0.32	0.48	0.28	0.52	†
along c (mm)	0.08	0.06*	0.32	0.03	†
Linear absorption coefficient (cm ⁻¹)	289	253	247	278	266
Minimum transmission coefficient	0.010	0.131	0.138	0.014	0.043
Maximum transmission coefficient	0.118	0.255	0.460	0.407	0.116
Maximum θ (°)	26	20‡	20	26	25
Scan time per step (s)	2	10	5	4	4
Number of regular reflections between check reflections	10	20	40	40	40
Check reflection intensity – final/initial	0.85	0.90	1.00	0.85	0.94
Number of reflections measured	390	246§	467	1369	1767
Number of independent reflections	329	240§	362	651	645
Number of independent reflections with $I > 2\sigma(I)$	329	240§	229	350	337

* These are along **a** and **c** for the pseudo-cell (see Table 1 and text).

† Complex shape – see text.

‡ For $hk0$ only, $\theta_{\max} = 30^\circ$.

§ Only pseudo-cell reflections measured – see text.

Solution and refinement

Dimethylthallium cyanide

The structure of the cyanide [see Fig. 1(a)] was arrived at by comparison with the known structure of the halides. The unit cell of the cyanide is very similar to those of the halides except that it is orthorhombic rather than tetragonal. It seems reasonable to assume that the orthorhombic distortion from tetragonal arises from atoms generally in the same positions as in the halides except that the cyanide groups are aligned parallel to **b**. Using the arguments discussed at length by Britton (1967) we would expect *b* to be about 0.5 Å

greater than *a* instead of the 0.1 Å we find here. Since it would seem that the spherical disorder of the cyanide groups is precluded by the orthorhombic symmetry, we would interpret the small difference between *a* and *b* as indicating large thermal motion of the cyanide group and also as probably precluding any possibility of end-to-end ordering (which would require space group *Imm2*). To attempt to decide these points from powder data seems hopeless. It would be of interest, but beyond our experimental means, to determine the cell constants as a function of temperature, since, if our view is correct, we would expect a tetragonal modification with completely

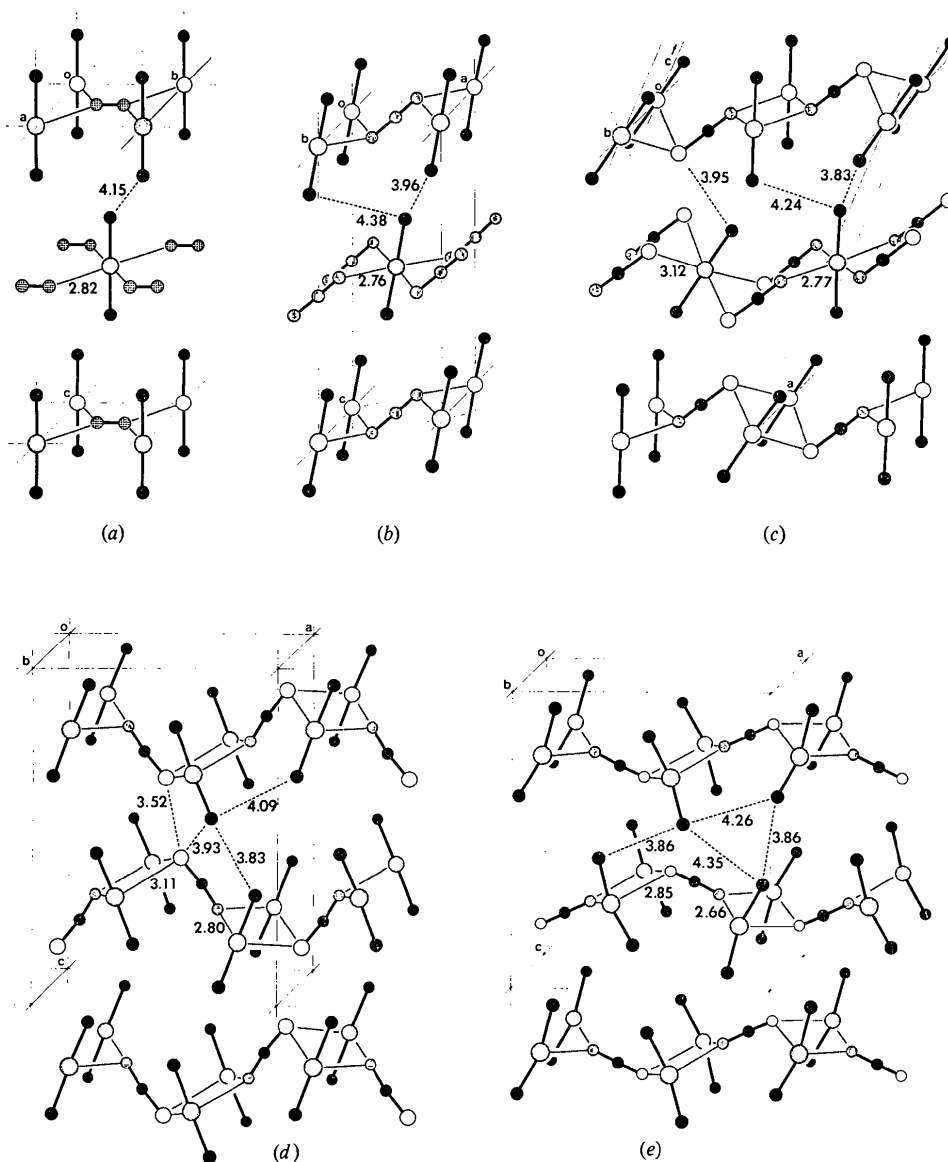


Fig. 1. The structures of dimethylthallium cyanide (a), azide (b), thiocyanate, monoclinic (c) and orthorhombic (d); and cyanate, orthorhombic (e). The large circles represent Tl and S atoms, the small circles, O (open), N (shaded), and C (black); hydrogen atoms are omitted. The thallium-ligand distances and some contact distances are given in Å.

disordered cyanide groups to appear at higher temperatures and the difference between a and b to become greater at temperatures below room temperature.

General

All of the remaining structures were solved from Patterson and Fourier maps and refined with anisotropic thermal parameters for the thallium atoms and isotropic thermal parameters for the remaining atoms. This choice was made from a study of the azide, where a comparison was made between anisotropic and isotropic thermal parameters for the light atoms. Hamilton's (1965) statistical test showed the additional parameters to be unjustified. For all of the structures the final parameters are given in Tables 3 and 4 and the structure factors are available.* No attempt was made to include hydrogen atoms.

Dimethylthallium azide

The refinement of the azide converged with $r=0.031$, $R=0.087$.†

Dimethylthallium thiocyanate (monoclinic)

An inspection of Fig. 1(c) will show that the thallium atoms alone can be put into a pseudocell that is similar to the cell of the azide, Fig. 1(b); this hindered the solution. A Raman spectrum, taken by R. S. Tobias and V. B. Ramos (Ramos, 1972), which showed two symmetric Tl-C stretching frequencies and two symmetric methyl deformation frequencies, helped us to find the correct cell. Refinement (based only on the pseudo-cell reflections) converged with $r=0.017$, $R=0.055$.

Dimethylthallium thiocyanate (orthorhombic)

This determination was straightforward; refinement converged with $r=0.045$, $R=0.112$. A generally featureless difference Fourier map, calculated at the end of the refinement, supported our original choice of $Pcma$ over $Pc2a$ as the space group.

Dimethylthallium cyanate (orthorhombic)

As with the structurally similar orthorhombic thiocyanate the space group was taken to be $Pcma$ at the start and no evidence was found at any later stage in the determination to contradict this. The one uncertain point in this structure is the orientation of the cyanate group. This same uncertainty occurs in the structure of the trigonal cyanate and we will consider both cases here. In each case one of the terminal atoms in the

cyanate group, atom A , is about 2.6 Å from each of two thallium atoms and the other terminal atom, atom B , is about 2.8 Å from each of two thallium atoms. It seems unlikely that the A atoms in the two structures are chemically different, so the question comes down to whether ACB is NCO or OCN . The Fourier and difference Fourier maps for both structures showed

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 exact 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
Azide				
Tl(a)	0	0	0	3.2
N(1)	$\frac{1}{2}$	$\frac{1}{2}$	0	4.0 (7)
N(2)	3384 (68)	$\frac{1}{2}$	497 (32)	5.1 (6)
C	-727 (86)	0	1538 (39)	5.4 (8)
Thiocyanate (monoclinic)				
Tl(1b)	0	0	0	3.5
Tl(2b)	$\frac{1}{2}$	0	$\frac{1}{2}$	3.2
S	2097 (16)	$\frac{1}{2}$	900 (16)	4.2 (3)
N	3475 (56)	$\frac{1}{2}$	3476 (56)	5.0 (12)
C(1)	2889 (64)	$\frac{1}{2}$	2367 (63)	4.4 (12)
C(2)	-434 (113)	0	-1743 (113)	8.5 (25)
C(3)	4243 (89)	0	5890 (88)	6.7 (19)
Thiocyanate (orthorhombic)				
Tl(c)	1576 (5)	0	1844 (4)	4.7
S	4666 (28)	$\frac{1}{2}$	3817 (23)	3.9 (7)
N	3157 (90)	$\frac{1}{2}$	2253 (69)	6.8 (29)
C(1)	3767 (92)	$\frac{1}{2}$	3037 (91)	4.7 (28)
C(2)	2363 (90)	0	531 (80)	2.2 (22)
C(3)	859 (59)	0	3237 (81)	-0.1 (17)
Cyanate (orthorhombic)				
Tl(d)	1162 (2)	0	2121 (3)	3.2
O	4482 (41)	$\frac{1}{2}$	3401 (49)	4.6 (12)
N	2578 (53)	$\frac{1}{2}$	2616 (55)	4.5 (14)
C(1)	3516 (56)	$\frac{1}{2}$	3014 (75)	3.7 (15)
C(2)	1600 (107)	0	587 (130)	11.3 (39)
C(3)	294 (92)	0	3517 (121)	9.4 (33)
Cyanate (trigonal)				
Tl(e)	353 (2)	$(1+x)/2$	-2033 (2)	3.5
O	0	7211 (22)	0	4.0 (7)
N	0	5885 (22)	0	2.8 (8)
C(1)	0	6558 (37)	0	3.5 (11)
C(2)	1661 (37)	$(1+x)/2$	-1678 (49)	3.5 (11)
C(3)	-888 (40)	$(1+x)/2$	-2942 (52)	4.5 (14)

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 except for Tl(e) where $\beta_{12} = \beta_{11}/2$ and $\beta_{23} = \beta_{13}/2$.

	β_{11}	β_{22}	β_{33}	β_{13}
Tl(a)	248 (7)	490 (13)	57 (2)	48 (2)
Tl(1b)	82 (4)	604 (31)	49 (3)	42 (3)
Tl(2b)	78 (4)	497 (28)	62 (3)	47 (3)
Tl(c)	145 (7)	482 (30)	47 (3)	-14 (8)
Tl(d)	49 (2)	557 (20)	54 (2)	-6 (3)
Tl(e)	44 (2)	36 (1)	82 (2)	2 (2)

* Supplementary Publication No. SUP 30956. See footnote on p. 1923.

† $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$; $R = \sum |F_o| - |F_c| / \sum |F_o|$. The numerator of r was the function refined. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), Vol. III, Table 3.3.1A; values for neutral atoms were used for all except thallium for which the Tl^+ values were used. Anomalous dispersion corrections from the same source (Table 3.3.2C) were used for thallium, $\Delta f' = -3.3$, $\Delta f'' = 11.0$.

negligibly different heights for the *A* and *B* atoms so a decision could not be made on this basis. However, it does appear possible to decide from the behavior of the isotropic temperature factors in refinement. The isotropic temperature factors B_A and B_B are (e.s.d.'s in parentheses): orthorhombic cyanate, $B_{A=N}$ and $B_{B=O} - 4.5(14)$ and $4.6(12)$, $B_{A=O}$ and $B_{B=N} - 5.9(16)$ and $2.3(11)$; trigonal cyanate, $B_{A=N}$ and $B_{B=O} - 2.8(8)$

and $4.0(7)$, $B_{A=O}$ and $B_{B=N} - 4.6(9)$ and $2.2(7)$. In both cases the $ACB=NCO$ arrangement gives a more reasonable set of isotropic thermal parameters and so we report the structure on this basis. It should be emphasized that while we regard this assignment as very probably correct, it is not certain. The least-squares refinement converged with $r = 0.050$, $R = 0.106$.

Dimethylthallium cyanate (trigonal)

With the cyanate group oriented as described in the previous section, refinement converged with $r = 0.023$, $R = 0.067$.

Results and discussion

The structures of the cyanide, azide, both modifications of the thiocyanate, and the orthorhombic cyanate are shown in Fig. 1. These structures are related to the dimethylthallium halide structures determined by Powell & Crowfoot (1934), but the relationship varies considerably in the series. The halide structure is tetragonal, in what can be regarded as a highly distorted sodium chloride structure, with layers characterized by $Tl-X$ contacts within the layers and $CH_3 \cdots CH_3$ contacts between the layers. This is essentially the structure of the cyanide [Fig. 1(a)] except that the tetragonal symmetry is distorted to orthorhombic because of the non-spherical shape of the cyanide group. The azide structure [Fig. 1(b)] is distorted further, to monoclinic symmetry, by the failure of the azide to be coplanar with the four neighboring thallium atoms. It is probable that the bonding here is essentially ionic and the distortion from coplanarity arises from packing considerations, but it should be noted that a very similar arrangement of four silver atoms and an azide group occurs in silver azide (Bassiere, 1935), which in turn is a distortion of the more symmetric and presumably more ionic potassium azide structure. On the other hand, if the $Tl-N$ bonds were strongly covalent, we would expect an allene-like arrangement of the thallium atoms around the azide

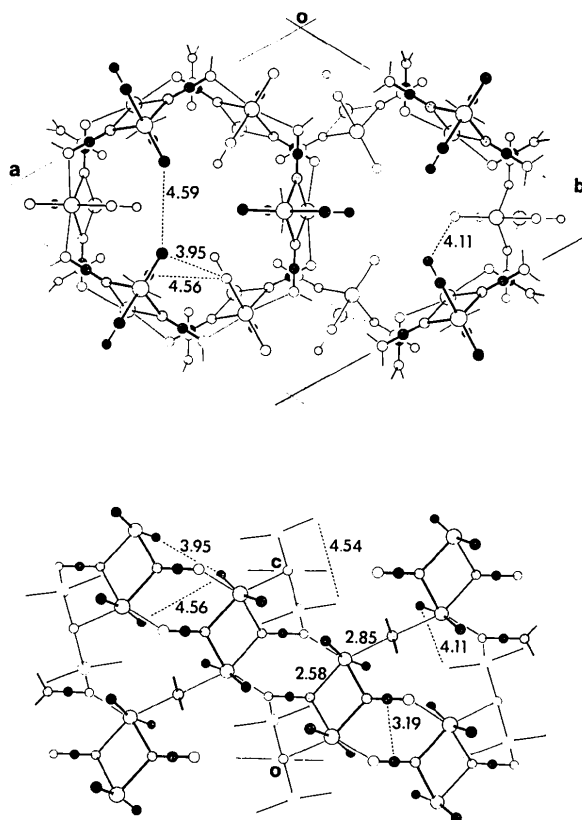


Fig. 2. The structure of trigonal dimethylthallium cyanate. Top: view down *c*; bottom: view along [110]. Details as in Fig. 1.

Table 5. Bond lengths (Å) and angles (°)

	Cyanide	Azide	Thiocyanate monoclinic	Thiocyanate orthorhombic	Cyanate orthorhombic	Cyanate trigonal
Tl—CH ₃ (1)			2.18 (12)	2.08 (11)	2.01 (17)	2.10 (7)
Tl—CH ₃ (2)		2.07 (5)	2.17 (9)	2.17 (11)	2.03 (15)	2.15 (7)
Tl—N (or CN)	2.82*	2.76 (3)	2.77 (4)	2.80 (6)	2.66 (4)	2.58 (3)
Tl—O					2.85 (3)	2.85 (4)
Tl—S			3.12 (1)	3.11 (2)		
N—N or N—C	(1.156)	1.17 (3)	1.22 (9)	1.31 (16)	1.16 (10)	1.23 (7)
C—O or C—S			1.60 (7)	1.48 (12)	1.18 (9)	1.19 (7)
CH ₃ —Tl—CH ₃	180	180	180, 180	177 (3)	166 (5)	166 (2)
N—Tl—N (or CN)	105*	98 (1)	102 (2)	102 (3)	101 (2)	78 (2)
O—Tl—O or S—Tl—S			87 (1)	89 (1)	92 (1)	128 (1)
Tl—N—Tl	105*	98 (1)	102 (2)	102 (3)	101 (2)	102 (1)
Tl—O—Tl or Tl—S—Tl			87 (1)	89 (1)	92 (1)	136 (2)
Tl—N—C or Tl—N—N	127*	114 (2)	121 (2)	118 (4)	129 (1)	129 (1)
Tl—O—C or Tl—S—C			99 (1)	100 (3)	120 (3)	112 (2)
N—C—X or N—N—N		180	179 (6)	170 (10)	179 (10)	180

* These parameters depend on the assumption that the $C \equiv N$ distance is 1.156 Å.

group. In the monoclinic thiocyanate [Fig. 1(c)] the arrangement is changed further in that the difference between the two ends of the thiocyanate group leads to alternate thallium atoms being chemically and crystallographically different with the consequence that the dimethylthallium groups are no longer related by translation and the unit cell is twice as large as before. Otherwise, the overall arrangement is basically the same as in the previous cases. The different ends of the thiocyanate are accommodated here by alternate TlN_4 and TlS_4 groups. In the orthorhombic modification [Fig. 1(d)] the thallium atoms are all equivalent, in a TlN_2S_2 group, but the dimethylthallium groups are not parallel since the C–N–Tl and C–S–Tl angles are different. The alternation of the orientation of the dimethylthallium groups again requires a doubling of the unit cell compared with the azide, and there is a further consequence that adjacent layers now do not pack together in the same way as in the earlier cases so that this can no longer be regarded as a distorted sodium chloride arrangement. The orthorhombic cyanate [Fig. 1(e)] is basically the same as the orthorhombic thiocyanate except that the C–N–Tl and C–O–Tl angles are significantly different from the corresponding angles in the thiocyanate so that the axial ratios are quite different.

The structure of the trigonal cyanate (Fig. 2) is quite different from those of all the others in this series. If we change the point of view from the preceding paragraph, we might alternatively describe the orthorhombic cyanate as involving infinite polymeric chains Tl–N–Tl–N– bound together into layers through the O–Tl interactions, with the layers combined into a three-dimensional arrangement through van der Waals and residual ionic interactions. [These Tl–N–Tl–N chains are parallel to the *b* axis and are roughly perpendicular to the page in Fig. 1(e)]. Corresponding to this we would describe the trigonal cyanate structure as involving Tl_2N_2 dimers bound together into a three-dimensional arrangement through the O–Tl interactions. This leads to a structure that is about 5% less efficient in packing but where presumably the bonding is more favorable. The detail where this is most apparent is the dihedral angle of 80° between the Tl–N–Tl plane and the Tl–O–Tl plane at opposite ends of the cyanate group. This is close to the 90° expected for an allene-like arrangement and, to the extent that the bonds are covalent, will allow stronger bonds to be formed than in the orthorhombic arrangement.

Bond lengths and angles are given in Table 5. All of the anions have normal bond lengths and angles within the large experimental errors. The dimethylthallium group is linear, either exactly or within experimental error, in the cyanide, azide, and both forms of the thiocyanate, but is significantly bent (14° away from linear) in the trigonal form of the cyanate; in the orthorhombic form of the cyanate the angle appears to be the same as in the trigonal form but the larger error allows the possibility of linearity. The wide variation in

CH_3 –M– CH_3 angles found with tin does not appear to be the case with thallium. If we assume that the bending in the cyanates does not appreciably affect the Tl– CH_3 bond length, then we can combine the seven independent measures of this bond length, properly weighted, to obtain $2.11(3)$ Å as our best estimate of this length.

The Tl–N distances are approximately equal at 2.8 Å in the cyanide, azide, and both thiocyanates. In particular the Tl–N distances are equal within experimental error in both forms of the thiocyanate as are the two Tl–S distances. This equality in the bond lengths in going from TlN_2S_2 to TlN_4 and TlS_4 for the thallium environment, as well as merely the existence of the two forms, suggests that the sulfur and nitrogen atoms compete about equally successfully for the bonding capacity of the thallium atom.

In contrast, the Tl–N distances in the two forms of the cyanate, about 2.6 Å, are shorter than in the thiocyanates, while the Tl–O distances are about 2.8 Å. This might be used as an argument that the nitrogen and oxygen atoms are mis-assigned, which was mentioned as a possibility in *Solution and refinement*. However, Blundell & Powell (1967) found in the structure of dimethyl-1,10-phenanthroline-thallium perchlorate, where the nitrogen and oxygen atoms are unambiguously identified, a similar situation. Their Tl–N distance is 2.57 Å and their Tl–O distance is 2.88 Å. Also, their N–Tl–N angle is 63° , constrained to be small by the geometry of the phenanthroline molecule, and the more or less unconstrained O–Tl–O angle is 135° ; these may be compared with an N–Tl–N angle of 78° in the trigonal cyanate, where the angle is constrained by the four-membered Tl_2N_2 ring, and an O–Tl–O angle of 128° . As a final comparison, the CH_2 –Tl– CH_2 angle is 168° compared with 166° in the trigonal cyanate.

Some of the shorter intermolecular distances are shown in Figs. 1 and 2. None is unusually short.

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References

- ALLEN, F. H., LERBSCHER, J. A. & TROTTER, J. (1971). *J. Chem. Soc. (A)*, pp. 2507–2509.
 BASSIÈRE, M. (1935). *C. R. Acad. Sci. Paris*, **201**, 735–737.
 BLUNDELL, T. L. & POWELL, H. M. (1972). *Proc. Roy. Soc. A* **331**, 161–169.
 BRITTON, D. (1967). *Perspect. Struct. Chem.* **1**, 109–171, especially p. 119 *et seq.*
 CHOW, Y. M. (1970). *Inorg. Chem.* **9**, 794–796.
 CHOW, Y. M. (1971). *Inorg. Chem.* **10**, 1938–1942.
 CHOW, Y. M. & BRITTON, D. (1975a). *Acta Cryst.* **B31**, 1929–1934.

- 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

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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