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The crystal structures of triethyltin cyanide and trimethyllead cyanide. By YEH MEI CHOW and DOYLE BRITTON,
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Triethyltin cyanide and trimethyllead cyanide are both orthorhombic with $a=11.89$, $b=14.76$, $c=5.97$ Å and $a=9.64$, $b=12.01$, $c=6.27$ Å, respectively. The space group is probably *Cmcm* in both cases, but this could not be conclusively demonstrated, since the complete structures were not determined in either case. The structures appear to be similar to that of trimethyltin cyanide, in which planar trimethyltin groups are linked by disordered cyanide groups aligned along the Sn---Sn direction. In each case the c -axis distance is also the Sn-C≡N-Sn distance.

The structure of $(\text{CH}_3)_3\text{SnCN}$ contains infinite chains of planar $(\text{CH}_3)_3\text{Sn}$ groups alternating with disordered CN groups aligned along the chain axis (Schlemper & Britton, 1966a). Two compounds that might be expected to have similar structures are $(\text{C}_2\text{H}_5)_3\text{SnCN}$ and $(\text{CH}_3)_3\text{PbCN}$. For neither compound was a complete solution of the structure possible; we report here the work done.

Triethyltin cyanide was prepared by mixing aqueous KCN with an ether solution of $(\text{C}_2\text{H}_5)_3\text{SnBr}$ and evaporating the ether layer (van der Kerk & Luijten, 1956); the melting point was 162–164° (reported, 163.5–164°). Needle-like crystals suitable for X-ray diffraction studies were grown by sublimation.

Trimethyllead cyanide was prepared by converting $(\text{CH}_3)_4\text{Pb}$ to $(\text{CH}_3)_3\text{PbCl}$ (Freidline & Tobias, 1966), reacting the chloride in aqueous solution with excess silver oxide to give a solution of $(\text{CH}_3)_3\text{PbOH}$, and passing gaseous HCN into the solution to give a precipitate of $(\text{CH}_3)_3\text{PbCN}$. Recrystallization from benzene produced two types of crystals, rectangular plates and very small needles. (Found: C, 17.11%; N, 5.22%; H, 3.24%. Calculated: C, 17.26%; N, 5.03%; H, 3.26%.) The crystals start to decompose around 110° and decompose completely by 285° without melting. The C–N stretching frequency occurs at 2134 cm^{-1} in the infrared and 2141 cm^{-1} in the Raman spectrum; these may be compared with the value of 2160 cm^{-1} in the infrared spectrum of $(\text{CH}_3)_3\text{SnCN}$. Infrared bands at 2930 and 3020 cm^{-1} indicate the presence of the methyl groups. The coupling constant $J(^{207}\text{Pb}-\text{CH}_3)$ is 85 in DMSO at room temperature, compared with $J=83$ for $(\text{CH}_3)_3\text{PbCl}$ and $J=154.5$ for $(\text{CH}_3)_2\text{PbCl}_2$ in DMSO (Shier & Drago, 1966).

A needle-like crystal of $(\text{C}_2\text{H}_5)_3\text{SnCN}$, elongated along c , and a plate-like crystal of $(\text{CH}_3)_3\text{PbCN}$, with greatest extension along c and with 110 and $\bar{1}\bar{1}0$ the developed faces, were examined with oscillation, Weissenberg, and precession photographs using Cu $K\alpha$ ($\lambda=1.5418$ Å) and Mo $K\alpha$ ($\lambda=0.7107$ Å) radiation. The cell constants are given in Table 1 along with those of $(\text{CH}_3)_3\text{SnCN}$. All three compounds have systematic extinctions $h+k$ odd in hkl and l odd in $h0l$ corresponding to *Cmcm* (the space group of the solved structure of $(\text{CH}_3)_3\text{SnCN}$), *C2cm*, or *Cmc2₁*. A powder photograph of the small needle-like crystals of $(\text{CH}_3)_3\text{PbCN}$ could be indexed completely using the cell constants and extinctions determined from the plate-like form. Spoon tests for pyroelectricity (Bunn, 1961) were negative for $(\text{C}_2\text{H}_5)_3\text{SnCN}$ and the needle-like form of $(\text{CH}_3)_3\text{PbCN}$, but positive for the plate-like form of the latter. Also, the plate-like form was twinned by 180° rotation about the normal to the 110 plane.

Table 1. Unit cell data

	$(\text{C}_2\text{H}_5)_3\text{SnCN}$	$(\text{CH}_3)_3\text{SnCN}$	$(\text{CH}_3)_3\text{PbCN}$
a	11.89 Å	9.96 Å	9.64 Å
b	14.76	11.96	12.01
c	5.97	6.06	6.27
Volume	1048 Å ³	722 Å ³	725 Å ³

Weissenberg (Cu $K\alpha$) and precession (Mo $K\alpha$) film intensity data were collected for $(\text{C}_2\text{H}_5)_3\text{SnCN}$. There was a very rapid decline in intensity with angle and only 108 independent reflections of measurable intensity could be collected. A Patterson map showed the Sn atom and the CN group to be in positions similar to those in $(\text{CH}_3)_3\text{SnCN}$, and also showed considerable electron density in or near the plane of the Sn atom perpendicular to the Sn–CN–Sn direction. This was confirmed by a Fourier synthesis, but all attempts to refine the ethyl carbon atom positions in all three of the possible space groups were unsuccessful even though group refinements were used with chemically reasonable starting models that more or less fit the electron density in the Fourier synthesis. The lack of success stems from the limited amount of data, which in turn is presumably a consequence of very large thermal motions, or rotational disorder in the $(\text{C}_2\text{H}_5)_3\text{Sn}$ positions, or both. There is no reason to doubt that the structure is basically the same as that in $(\text{CH}_3)_3\text{SnCN}$, but we have not proved this nor do we think it possible without low temperature data.

No attempt was made to measure the intensities of the reflections of the $(\text{CH}_3)_3\text{PbCN}$. The relative intensities of the reflections were very similar to those in $(\text{CH}_3)_3\text{SnCN}$ and the Pb atom position is surely similar to that of the Sn. The main reasons for doubt about the structure are the positive pyroelectric effect shown by the plate-like form and the unusual growth and twinning of this form. These are anomalies we cannot explain, but the existence of the needle-like form, with the same cell constants, which does not show a pyroelectric effect, leads us to believe that at least this form has the same structure as the Sn compound. It should be noted that in $(\text{CH}_3)_3\text{GeCN}$, where there are ordered, tetrahedral molecules still with CN groups aligned along the Ge---Ge line, the space group is not *Cmc2₁*, which might be expected from introducing a tetrahedral distortion into the *Cmcm* structure, but *Pmn2₁*, with a cell approximately half as large (Schlemper & Britton, 1966b).

In the absence of the complete structure determination, what we know are the M---M distances (M=Sn, Pb). In each case this distance is the sum of the M–C, C–N, and N–M distances. The M–C and M–N distances are certainly

different, and if the space group in either compound is indeed $Cmc2_1$, they may be very different; the best we can do is to report the averages, which we will call the M-CN distances. If we assume that the C-N distance is 1.16 Å (Britton, 1967), then we calculate from the c values for the average M-CN distances, 2.45, 2.40, and 2.55 Å for $(CH_3)_3SnCN$, $(C_2H_5)_3SnCN$, and $(CH_3)_3PbCN$, respectively. The difference between the first two numbers is an indication of the sensitivity of this bond distance to the environment. The difference between the first and third is what we would expect from the univalent radii for Sn^{4+} and Pb^{4+} , 0.96 and 1.06 Å, respectively (Pauling, 1960).

In the absence of low temperature facilities we do not anticipate any further work on either of these compounds.

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Polytypism and spiral growth in cadmium iodide. By M.R. TUBBS, *School of Physics, University of Warwick, Coventry CV4 7AL, England*

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A new measurement of the refractive index of CdI_2 has been used to re-evaluate the step heights of growth spirals on the surfaces of CdI_2 crystals reported by Trigunayat & Verma. There is now good correlation between step heights and crystal structure since the corrected step height is an integral multiple of the c dimension of the unit cell for 30 out of 36 spirals on 33 crystals with polytype structures having between two and twenty iodide layers in the unit cell.

A careful study of polytypism in cadmium iodide was reported by Trigunayat & Verma (1962) who used an interference technique to measure the step heights of growth spirals on the surfaces of CdI_2 single crystals whose structure type was then determined by X-ray diffraction. They concluded that in most crystals there was no correlation between step height and the c dimension of the unit cell determined by X-ray methods. The step heights were measured by the internal interference method (Forty, 1952) which gives the optical height of a step (*i.e.* height \times refractive index). A value of 1.849 ± 0.001 was used for the ordinary refractive index of CdI_2 at the wavelength of the mercury green line $\lambda = 5461$ Å. (The ordinary refractive index is appropriate for microscope observations, using narrow pencil

illumination, of CdI_2 platelets with c axes perpendicular to their habit plane.)

Recent studies of the refractive index and dispersion of CdI_2 by interference methods (Tubbs, 1969; Lee, Said, Davies & Lim, 1969) show that the ordinary refractive index at $\lambda = 5461$ Å is 2.39 ± 0.04 and the birefringence 0.2. This value is also consistent with 2.5 ± 0.1 quoted by Fotland (1959) for observations in 'white light'. A more accurate value for the ordinary index may be obtained from measurements of step heights since all steps must be integral multiples of $M = 6.84$ Å, the thickness of the basic I-Cd-I layer.

A set of step height measurements is shown in Table 1 for eight crystals where the steps were less than 15 I-Cd-I

Table 1. *Corrected step heights (using refractive index of 2.41) for small steps on CdI_2 crystals where the step height is known to an accuracy of ± 0.26 basic layers or better*

Crystal number	Step height* in multiples of $M = 6.84$ Å	Corrected step height (units of M)	Structure type
24	19.33 ± 0.26	14.8	4H
35	12.00 ± 0.22	9.2	unidentified
37	13.09 ± 0.26	10.0	unidentified
42	13.71 ± 0.22	10.5	resembles 4H
47	17.01 ± 0.05	13.0	resembles 2H
56	10.29 ± 0.25	7.9	16H
62	18.19 ± 0.12	14.0	2H + 14H
66	15.66 ± 0.23	12.0	22H

* From Trigunayat & Verma (1962)

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