Raman and *X*-Ray Crystallographic Studies of Solid Trimethylindium

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We have re-determined the crystal and molecular structure of trimethylindium, confirming that it adopts a tetrameric form in the crystal. Improved data at 273 K allow a better description of the intermolecular interactions, which involve the sharing of one methyl group of each molecule in forming the tetramer, which has $\bar{4}$ (S_4) symmetry, and a weaker interaction through another methyl group linking the tetramers into an infinite three-dimensional network. The overall co-ordination at indium may be described as trigonal bipyramidal, with the shortest InC bonds in the equatorial plane. The Raman spectrum of the crystalline solid shows bands close to those reported for the liquid, but there are splittings for some of the *e'* modes that are consistent with the loss of three-fold symmetry in each molecular unit; no clear evidence for any additional bands that might be ascribed to the intermolecular links is found. A metastable, apparently amorphous phase was prepared by rapid evaporation of the solid and condensation at −46 °C. Its Raman spectrum still shows the loss of three-fold symmetry, but is less complex than that of the crystal, suggesting that the rapidly sublimed solid lacks the clear-cut tetramers found in the crystal, but has more substantial intermolecular interactions than occur in the liquid. No evidence for any other more stable crystalline phase was found.

Trimethylindium was first prepared in 1934[1] and its infrared spectrum as a gas and its Raman spectrum as a heated liquid have been investigated.[2] A crystal structure of limited accuracy was briefly reported,[3] showing that the trigonal planar co-ordination of the indium by three methyl groups in the isolated molecule was supplemented in the crystal by a long contact with one methyl group of a neighbouring molecule, which linked the molecules into loose tetramers, and by a further longer contact with a methyl group belonging to a molecule in a neighbouring tetramer, which linked the tetramers into a three-dimensional array throughout the crystal.

Recently, the substance has attracted considerable attention as a source of indium atoms in thin-film growth techniques for the production of materials of controlled composition and semiconducting properties, and its physical properties have come under renewed scrutiny.[4] It has been suggested that another solid form exists that has a lower vapour pressure than the normal crystal, and is therefore thermodynamically more stable. We have studied the Raman spectrum of the solid after various sublimation procedures *in vacuo*, hoping to find evidence for this putative second phase, and have studied a crystalline sample by *X*-ray diffraction both to investigate the possibility of the existence of a second solid phase and to confirm the reported crystal structure with its network of bridging methyl groups.

Our results show no sign of any second phase, either at room temperature after varying sublimation regimes or at lower temperatures. The Raman spectrum of the solid is more complex than that reported for the liquid, and this is shown to be consistent with the intermolecular interactions. New *X*-ray data provide a substantially improved crystal structure at 273 K which confirms the essential correctness of the earlier report but, being considerably more accurate, allows better definition of the geometry of the methyl group binding.

Experimental

The sample (provided by Professor D. C. Bradley of Queen Mary College) was sealed in a fused quartz ampoule, within which it remained while all the Raman data were obtained. This guaranteed the absence of any contamination by air or water-reaction products. Raman spectra were recorded using a Spex Ramalog double spectrometer with Ar^+ laser excitation at 514.5 nm; the sample was at room temperature while the spectra were run but was subjected to various heating or cooling regimes to transfer part of it from one arm of the sample ampoule to the other, with condensation at room temperature, at liquid nitrogen temperature, or at an intermediate cool temperature. It was found possible to condense the sample either as a polycrystalline film or as an apparently amorphous film, but the Raman spectra showed no significant difference in the numbers and positions of the bands. At room temperature the spectrum of the amorphous sample reverted to that of the polycrystalline phase within an hour or two, showing that the latter was thermodynamically stable. The Raman bands observed for 'crystalline' and 'amorphous' solids are listed in Table 1, with the reported[2] Raman bands of the liquid and gas-phase i.r. bands for comparison.

X-Ray Crystallography.—For the *X*-ray study portions of the sample were transferred to Pyrex capillaries by sublimation under vacuum and sealed without introduction of any inert atmosphere. A single crystal of trimethylindium was grown in one of these capillaries by thermal cycling between 263 and 320 K; when a crystal of sufficient size was obtained at 263 K the temperature was held at 273 ± 0.1 K to prevent further growth. Low temperature control was achieved using an Oxford Cryosystems low temperature device.[5]

Crystal data. C_3H_9In, $M = 159.92$, tetragonal, space group $P4_2/n$, $a = 13.216\,6(11)$, $b = 6.403\,9(9)$ Å, $U = 1\,118.6$ Å^3 [from 2θ values of 60 reflections measured at $\pm\omega(2\theta = 28$—$32°$, $\lambda = 0.710\,73$ Å)], $Z = 8$, $D_c = 1.899$ g cm^{-3}, $T = 273$ K, colourless tabular crystal, 0.230 × 0.230 × 0.116 mm, $\mu = 4.00$ mm^{-1}, $F(000) = 608$.

Data collection and processing. Stoë STADI-4 four-circle diffractometer, graphite-monochromated Mo-K_α *X*-radiation, $T = 273$ K, ω–2θ scans with ω scan width $(0.99 + 0.347 \tan\theta)°$, 1 090 unique data ($2\theta_{max.}$ 50°, h 0 to 15, k 0 to 15, l 0 to 7), initial

Table 1. Vibrational spectra of trimethylindium (band positions in cm^{-1})

Raman crystal	Raman frost	Raman liquid*	I.r. gas*	Assignment
86				
125		132		$\nu_{17}\ e'$
155				
462vs	463vs	467vs(p)		$\nu_3\ a_1'$
480m				
488s	490s	495s(dp)	500s	$\nu_{16}\ e'$
498s	497s			
		635w(dp)		$\nu_{20}\ e''$
			687ms	$\nu_9\ a_2''$
		725w(dp)	725s	$\nu_{15}\ e'$
1 094m	1 105m(br)	1 116m(br,dp)		$\nu_{14}\ e'$
1 123m				
1 151s	1 153s	1 157s(p)	1 155vw	$\nu_2\ a_1'$
		2 861w(sh)	2 860m	?
2 915m		2 910ms(p)	2 920s	$\nu_s(CH_3)$
2 975mw(br)		2 974mw(dp)		
			3 000s	$\nu_{as}(CH_3)$

* Ref. 2; p = polarised, dp = depolarised.

Table 2. Atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
In	0.285 50(7)	0.504 11(6)	0.413 86(14)
C(1)	0.154 9(9)	0.430 3(9)	0.272 7(21)
C(2)	0.350 0(10)	0.626 5(9)	0.246(3)
C(3)	0.337 6(9)	0.456 2(11)	0.713 7(21)
H(1A)	0.099 5(9)	0.403 4(9)	0.383 6(21)
H(1B)	0.198 3(9)	0.367 1(9)	0.214 3(21)
H(1C)	0.116 8(9)	0.467 2(9)	0.144 4(21)
H(2A)	0.383 3(10)	0.672 8(9)	0.367(3)
H(2B)	0.297 2(10)	0.671 3(9)	0.157(3)
H(2C)	0.408 9(10)	0.598 5(9)	0.145(3)
H(3A)	0.411 3(9)	0.491 4(11)	0.709 4(21)
H(3B)	0.345 8(9)	0.375 2(11)	0.697 8(21)
H(3C)	0.301 3(9)	0.473 2(11)	0.860 7(21)

Table 3. Bond lengths (Å), angles (°), and torsion angles (°) with e.s.d.s in parentheses

In–C(1) 2.179(12) In–C(2) 2.121(14) In–C(3) 2.136(13)

C(1)–In–C(2)	116.8(5)	In–C(2)–H(2A)	103.5(12)
C(1)–In–C(3)	119.7(5)	In–C(2)–H(2B)	115.2(13)
C(2)–In–C(3)	123.5(5)	In–C(2)–H(2C)	109.5(12)
In–C(1)–H(1A)	114.3(11)	In–C(3)–H(3A)	98.0(11)
In–C(1)–H(1B)	93.9(10)	In–C(3)–H(3B	104.0(11)
In–C(1)–H(1C)	118.8(11)	In–C(3)–H(3C)	125.3(12)
C(2)–In–C(1)–H(1A)	−145.6(11)	C(3)–In–C(2)–H(2A)	−24.8(14)
C(2)–In–C(1)–H(1B)	101.0(10)	C(3)–In–C(2)–H(2B)	−144.3(13)
C(2)–In–C(1)–H(1C)	−13.8(14)	C(3)–In–C(2)–H(2C)	91.8(13)
C(3)–In–C(1)–H(1A)	31.6(13)	C(1)–In–C(3)–H(3A)	164.2(10)
C(3)–In–C(1)–H(1B)	−81.8(11)	C(1)–In–C(3)–H(3B)	51.7(13)
C(3)–In–C(1)–H(1C)	163.4(11)	C(1)–In–C(3)–H(3C)	−75.0(15)
C(1)–In–C(2)–H(2A)	152.3(11)	C(2)–In–C(3)–H(3A)	−18.8(13)
C(1)–In–C(2)–H(2B)	32.8(15)	C(2)–In–C(3)–H(3B)	−131.3(11)
C(1)–In–C(2)–H(2C)	−91.1(13)	C(2)–In–C(3)–H(3C)	102.0(15)

absorption correction by means of 72 ψ scans (minimum and maximum transmission factors 0.331, 0.444 respectively), giving 450 with $F > 6\sigma(F)$ for use in all calculations. No significant crystal decay or movement.

Structure solution and refinement. The positions of the C atoms were located from a difference Fourier calculation using the published[3] In co-ordinates. Iterative cycles of least-squares refinement and difference Fourier synthesis gave the positions of the H atoms. At isotropic convergence, final correction for absorption was made using DIFABS[6] (minimum and maximum corrections 0.803, 1.255 respectively). Refinement of the structure (by least-squares on *F*)[7] with anisotropic thermal parameters for In and C, and with H atoms in rigid methyl groups with fixed U_{iso} = 0.08 Å^2 converged to *R*, *R'* = 0.0335, 0.0338 respectively, *S* = 1.141 for 47 refined parameters and the final ΔF synthesis showed no peak above 0.45 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,081\ F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max.}$ was 0.037. A secondary extinction coefficient refined to 23(10) × 10^{-9}. Molecular geometry calculations utilised CALC[8] and the Figures were produced using ORTEP[9] and PLUTO.[10]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results

When *X*-ray data collection was complete, the unit cell dimensions were determined on the diffractometer at 273 K and at successively lower temperatures (233, 193, 153 K) as the sample was cooled in a jet of cold nitrogen.[5] No changes were observed other than those compatible with a steady contraction of the unit cell as the temperature dropped. When the temperature reached 113 K the crystal was lost, as it detached itself from the wall of the tube, presumably because of the effects of differential contraction. Further attempts to cool a crystal to 100 K so that a more precise low temperature structure could be determined also failed for the same reason. At no stage in the cooling and warming cycles used to induce growth of the crystals was there any sign of the existence of any other crystalline phase. The crystal and molecular structure was determined from the data collected using the first crystal at 273 K, as detailed above. The atomic co-ordinates are listed in Table 2, with bond lengths and angles for the individual molecule in Table 3, and intermolecular geometry in Table 4. The tetramer is shown in Figure 1, which also indicates the atom numbering scheme adopted, and the packing of tetramers in the crystal is shown in Figure 2.

Description of the Structure of Trimethylindium

The solid state structure of $InMe_3$ comprises molecules which are bound into cyclic tetramers by intermolecular In $\cdots$ C(1) contacts of 3.083(12) Å. These tetramers, in which each In is 4.41 Å out of the plane of the other three, have crystallographic $\bar{4}$ (S_4) symmetry, and each is linked by four longer In $\cdots$ C(2) intermolecular contacts of 3.558(15) Å to four others to give an infinite three-dimensional structure. Since these contacts are approximately normal to the InC_3 molecular plane the indium co-ordination could be described as axially-elongated trigonal bipyramidal. The molecules lie in general positions and have no required symmetry.

The effects of the crystal environment on the internal geometry of the molecule can be seen in the In–C bond distances: C(1), which participates in the closer In $\cdots$ C contact, has a bond length of 2.179(12) Å to In, longer by 2.5σ than the In–C(2) and In–C(3) distances of 2.121(14) and 2.136(13) Å respectively. Although the C–In–C angles are significantly different from 120°, their sum of 359.94° indicates an essentially planar InC_3 skeleton. Apparent InCH angles range from 93.9(10) to 125.3(12)°, and the closest In $\cdots$ H contact is 2.50 Å. The methyl group orientations display no symmetry in each molecule. It may be noted that there is no significant difference between the In–C(2) and In–C(3) bond distances in the redetermined structure, although these were originally reported[3]

Table 4. Intermolecular structural parameters (distances in Å, angles in °) with e.s.d.s in parentheses

		In···C(1′)	3.083(12)	In···C(2″)	3.558(15)
C(1′)···In–C(1)	91.5(4)	C(1′)···In–C(2)	94.3(5)	C(1′)···In–C(3)	86.9(4)
C(2″)···In–C(1)	91.3(4)	C(2″)···In–C(2)	97.3(5)	C(2″)···In–C(3)	79.2(4)
In···C(1′)–In′	168.1(6)	In···C(2″)–In″	166.2(6)	C(1′)···In···C(2″)	165.4(3)

Singly and doubly primed atoms are related to their unprimed equivalents by the symmetry operations $(y, \frac{1}{2} - x, \frac{1}{2} - z)$ and $(y - \frac{1}{2}, 1 - x, \frac{1}{2} + z)$ respectively.

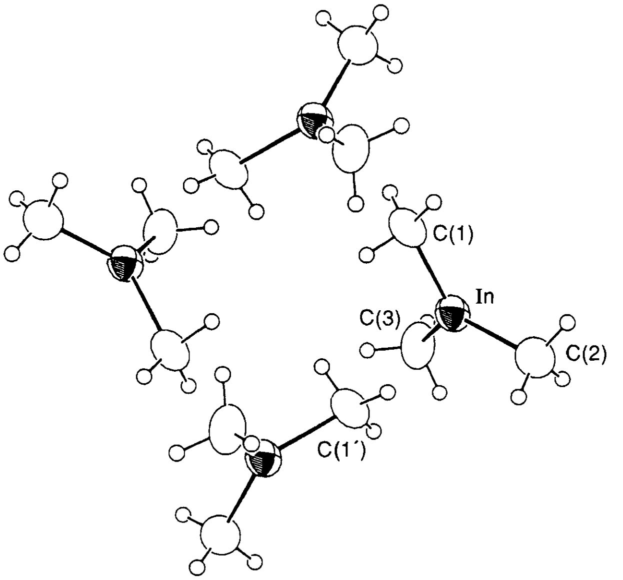

Figure 1. ORTEP view of one tetrameric unit showing crystallographic $\bar{4}$ symmetry and the numbering scheme adopted. Thermal ellipsoids are drawn at the 30% probability level, except for the hydrogen atoms which have artificial radii of 0.10 Å for clarity. The primed label has the same significance as in Table 4

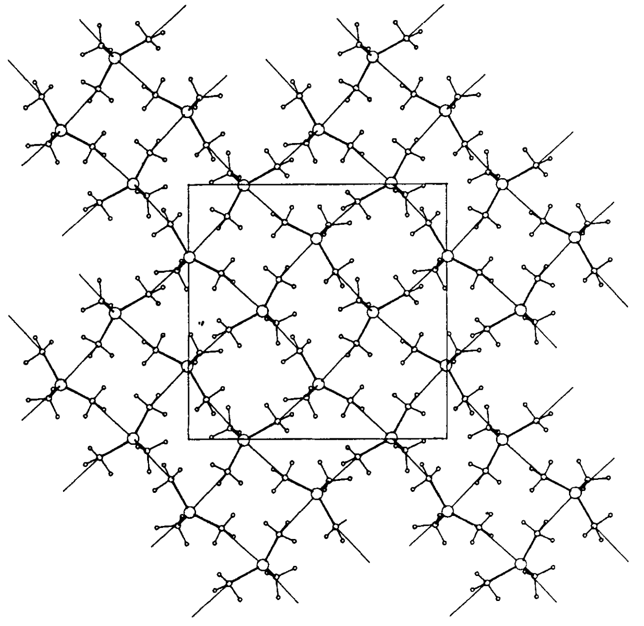

Figure 2. PLUTO plot of the three-dimensional network viewed along the *c*-axis: symmetry operations are defined in Table 4

as 2.12 and 2.06 Å respectively. The three-fold improvement in precision in our results reveals that the apparent difference is probably illusory, even though C(3) takes part in no additional bonding whereas the long contacts between tetramers occur through C(2).

The Raman spectrum observed for large, apparently crystalline chunks of solid in the original sample contained bands as listed in Table 1. With a single crystal and the strongly directional characteristics of a laser Raman spectrometer it is hard to be sure that spectra obtained are representative of a general orientation of the crystal, but no significant differences were found when the sample positioning in the beam was altered. The bands seen clearly correspond to those reported earlier for the liquid, but there are distinct splittings, especially in the region assigned to In–C stretching modes, near 500 cm^{-1}. The liquid data are given in Table 1 for comparison, together with gas-phase i.r. band positions, both from ref. 2. The spectrum of material newly-condensed in an apparently polycrystalline film was identical to that found for the original large crystals, which tends to confirm the absence of significant orientation effects.

When the sample was evaporated rapidly and condensed at an intermediate temperature (−46 °C, maintained with a chlorobenzene slush bath) an apparently amorphous film resulted, whose Raman spectrum was less complex than that of the crystalline material but contained bands in the same regions. It was also similiar to the spectrum of the liquid, but with a distinct splitting in the In–C stretching region in particular. There was no sign of the development of new bands or the loss of important regions of the spectrum, as might have been expected if the molecular structure or the intermolecular bonding had changed in any important fashion. Over a period of an hour or so, while the spectrum was recorded at room temperature, the spectrum reverted to that of the polycrystalline material, showing that the amorphous condensate was thermodynamically less stable than the crystal, and that the conversion was slow at room temperature, but not very slow.

The Raman studies on the crystalline solid are consistent with a distortion of the molecule from the D_{3h} symmetry of the isolated molecule. The InC stretching bands in particular show two components (a_1' and e') in the liquid, but the higher frequency band splits into two components in the crystal (Table 1), confirming that this is the e' mode, as suggested[2] on the basis of polarisation measurements in the liquid, and that the three-fold degeneracy is lost. A weaker component at slightly lower frequency appears as well; it is much harder to be certain what causes this. It might be due to the coupling of molecular modes between members of the tetrameric unit, or to the fourth InC bond formed within the tetramer, or of course it could be due to a chance coincidence of an overtone or combination band with the InC bond stretching region, revealed in the solid because of the sharpness of the main bands. Another splitting appears in the band near 1 100 cm^{-1}, assigned[2] to the antisymmetric combination of methyl deformations, e'. Again, this is consistent with the reduction in symmetry, but does not tell us more about the interactions.

In the −46 °C frost, which seems to be a metastable amorphous material, the main features of the spectrum are retained, but the splitting of the *e′* methyl deformation band is not seen, though that in the InC *e′* band remains. Apart from this, the spectrum is very similar to that reported for the liquid. It seems likely that the amorphous frost is condensed from the gas phase so fast that the tetrameric structure does not have time to form in a regular fashion, but that each molecule accepts additional interactions from one or more neighbouring methyl groups in much the same way as in the crystal; the symmetry of each molecule is thus reduced with loss of the three-fold degeneracy, but the bands are broader than in the crystal, showing that a range of environments is present, rather than a single fixed structure. The network of intermolecular interactions must then be able to rearrange slowly at room temperature, as the Raman spectrum transforms gradually to that of the crystal.

In the low frequency region of the spectrum, below 200 cm^{-1}, we find several broad bands (Table 1). The study of the liquid reported a single band assigned to the *e′* InC_3 deformation at 132 cm^{-1}, and this mode is presumably involved in the solid bands as well. It has not proved possible to analyse the rather few bands observed in terms of the expected modes of the tetramer in any unique fashion. The spectrum of the −46 °C frost was not identical with that of the crystal in this region, but again the differences did not lend themselves to any unique interpretation.

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References

1 L. M. Dennis, R. W. Work, and E. G. Rochow, *J. Am. Chem. Soc.*, 1934, **56**, 1047.
2 J. R. Hall, L. A. Woodward, and E. A. V. Ebsworth, *Spectrochim. Acta*, 1964, **20**, 1249.
3 E. L. Amma and R. E. Rundle, *J. Am. Chem. Soc.*, 1958, **80**, 4141.
4 D. C. Bradley, personal communication.
5 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
6 DIFABS, program for empirical absorption corrections, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
7 SHELX 76, program for crystal structure refinement, G. M. Sheldrick, University of Cambridge, 1976.
8 CALC, program for molecular geometry calculations, R. O. Gould and P. Taylor, University of Edinburgh, 1985.
9 ORTEP II, interactive version, P. D. Mallinson and K. W. Muir, *J. Appl. Crystallogr.*, 1985, **18**, 51.
10 PLUTO, W. D. S. Motherwell, University of Cambridge, 1976.

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