Crystal Structure of Acetato(dimethyl)indium(III)

By **F. W. B. Einstein,* M. M. Gilbert, and D. G. Tuck,‡** Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada

Crystals of the title compound are orthorhombic, $a = 7{\cdot}265(2)$, $b = 7{\cdot}325(2)$, $c = 13{\cdot}286(5)$ Å, $Z = 4$, space group *Pnma*. The structure was determined from *X*-ray counter data and refined by full-matrix least-squares calculations to *R* 0·040 for 527 observed reflections. The six-co-ordinate indium lies on a mirror plane and is bonded to two approximately *trans*-methyl groups, which also lie in the mirror plane, and four oxygen atoms. A bidentate acetate group lies across the mirror plane, with In–O 2·371(5) Å, while two weaker bridging contacts from different adjacent acetate groups with In–O 2·600(5) Å, serve to link the structure as a linear polymer. These bond length differences are unexpected since in a compound of this type the bridge bonds would be expected to be shorter than those of the bidentate acetate.

THERE was a lack of information of the preparative and structural properties of the organoindium compounds.[1] Although an increasing amount of preparative work has been reported recently, until this present study only three indium(III) organometallic compounds had been subjected to *X*-ray structural analysis, namely trimethyl-,[2] triphenyl-,[3] and tris(cyclopentadienyl)-indium(III).[4] Each of these show interesting features, and in particular the co-ordination number of the indium atom exceeds three in each case. This is in keeping with the properties of indium in its purely inorganic co-ordination chemistry.[5]

Acetatodimethylindium(III) was first prepared[6] as part of a study of the derivatives of the dimethyl indium halides, by the reaction of acetic acid and trimethylindium. It was purified by sublimation, but unfortunately was insufficiently soluble in benzene for a molecular-weight determination to be made. We have carried out further investigations on this compound as part of a study of the acetates of indium;[7] one preliminary conclusion from the preparative and spectroscopic results was that the compound is polymeric in the solid state, a property which is apparently shared with other derivatives of indium(III) acetate. A further interesting feature is that the mass spectrum of acetato(dimethyl)indium shows a small peak corresponding to the presence of the dimer, as well as those related to the single monomeric unit, which suggests that polymerization in the solid state persists to some extent in the vapour.

In view of these interesting properties, it seemed worthwhile to carry out a single-crystal *X*-ray structural investigation which we now report. As this work was being completed, the structures of diethyl(thioacetato)-indium(III), $Et_2(MeCOS)In^{III}$, and diethyl(acetato)-indium(III), $Et_2(AcO)In^{III}$, were published.[8,9]

EXPERIMENTAL

The crystals were white needles, elongated in the *b* direction. The space group was determined from Weissenberg photographs of layers $h0$—$2l$ and precession photographs of layers $0kl$, $1kl$, and $hk0$, taken with Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å).

Crystal Data.—$C_4H_9InO_2$, $M = 203{\cdot}8$, Orthorhombic, $a = 7{\cdot}265(2)$, $b = 7{\cdot}325(2)$, $c = 13{\cdot}268(5)$ Å, $U = 706$ Å^3, $D_m = 1{\cdot}92$ (flotation), $Z = 4$, $D_c = 1{\cdot}92$, $F(000) = 392$, Mo-$K_{\alpha 1}$ radiation, $\lambda = 0{\cdot}70926$ Å, μ(Mo-K_α) = 33 cm^{-1}. Space group *Pnma* or $Pn2_1a$ from systematic absences: $0kl$ when $k + l$ is odd, $hk0$ when h is odd.

A needle-shaped crystal with dimensions 0·06 × 0·35 × 0·07 mm was used for the measurement of cell dimensions and data collection. To minimize intrinsic multiple scattering, the b^* axis was offset *ca.* 4° from the ϕ axis of the diffractometer. All dimensions were determined from the least-squares analysis of 2θ values for 12 reflections, with $2\theta > 33°$ the centring of reflections and measurement of angles was done on a computer-controlled Picker four-circle diffractometer with Mo-K_α radiation and a take-off angle of 1·4° at 23 °C.

Intensity data for one octant of the reciprocal lattice were collected by the θ—2θ scan technique with niobium filtered Mo-K_α radiation and a scintillation counter equipped with a pulse-height discriminator. The take-off angle was 3°. Each reflection was scanned for 1·5° in 2θ (extended for the $\alpha_1 - \alpha_2$ splitting) at a scan rate of 2° min^{-1}, and the background counted for 20 s at each end of the scan range. Every 50 reflections, two standard reflections were measured. There was a linear decrease of intensity, to a maximum of *ca.* 5%, over the data collection period; appropriate corrections to the intensities were applied. In this manner, intensities for the 684 reflections with $2\theta < 50°$ were measured.

The reflection intensity is given by $I = P - t_p/t_B(B_1 + B_2)$ and the standard deviation of an intensity $\sigma(I)$, was defined by: $\sigma(I) = [P + (t_p/t_B)^2(B_1 + B_2) + (kI)^2]^{\frac{1}{2}}$, where P is the peak count, scanned for t_p seconds, B_1 and B_2 are the two backgrounds, each measured for $\frac{1}{2}t_B$ seconds, and k is an 'instability factor,' which was assigned a value of 0·03 in

---

‡ *Present address:* Department of Chemistry, University of Windsor, Windsor 11, Ontario, Canada.

[1] G. E. Coates and K. Wade, 'Organometallic Compounds,' vol. 'The Main Group Elements,' Methuen, London, 1967, p. 361.

[2] E. L. Amma and R. E. Rundle, *J. Amer. Chem. Soc.*, 1958, **80**, 4141.

[3] J. F. Malone and W. S. McDonald, *J. Chem. Soc.* (*A*), 1970, 3362.

[4] F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, *Inorg. Chem.*, 1972, **11**, 2832.

[5] D. G. Tuck, Proc. C.N.R.S. Conf. No. 191, 'La Nature et les Propriétés des Liaisons de Co-ordination,' Editions du C.N.R.S., Paris, 1970, p. 159.

[6] H. C. Clark and A. L. Pickard, *J. Organometallic Chem.*, 1967, **8**, 427.

[7] J. J. Habeeb and D. G. Tuck, preceding paper.

[8] H.-D. Hausen, *Z. Naturforsch.*, 1972, *B*, **27**, 82.

[9] H.-D. Hausen, *J. Organometallic Chem.*, 1972, **39**, C37.

this case. Reflections having $I < 2{\cdot}3\sigma(I)$ were considered unobserved and were not used in the structure solution and refinement. The 527 observed and 157 unobserved reflections were corrected for Lorentz and polarization factors and a set of $|F_o|$ values, on a relative scale, were thus obtained. The standard deviation of an observed structure factor, $\sigma(|F_o|)$, was defined as $\sigma(|F_o|) = \sigma(I)/2\mathrm{Lp}|F_o|$.

Structure Solution and Refinement.—The position of the indium atom was found from a three-dimensional Patterson map. A subsequent three-dimensional electron-density synthesis phased by the indium atom lying on the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ along *b*, located all the nonhydrogen atoms, and indicated anisotropic motion for the indium atom.

The structure was refined by conventional, full-matrix least-squares methods. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where weights w are $1/\sigma^2(|F_o|)$. (Unit weights were used in the early stages of refinement, until all atoms were no longer undergoing significant shifts.) Values for the scattering factors were taken from ref. 10, and anomalous dispersion corrections to the scattering factors for indium were included in the structure-factor calculations.

Four cycles of least-squares refinement, with the indium atom assigned anisotropic thermal parameters of the form $\exp[-(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$ and the other atoms isotropic, and with the assumed centrosymmetric space groups, led to R 0·053 and a weighted residual R' of 0·060 $\{R' = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. Two further cycles of refinement with all atoms assigned anisotropic temperature factors resulted in convergence with R 0·040 and R' 0·044.

The last cycle of refinement showed no parameter shift $>0{\cdot}05\sigma$. The highest peak in the difference-Fourier function computed at this point was 0·5 eÅ^{-3}, with the highest peaks surrounding the indium atom. No conclusive evidence for hydrogen-atom location could be found at any stage of the refinement, so these atoms were not included.

The thermal motion appeared less pronounced normal to the mirror plane and careful examination of the difference-Fourier map showed no unusual features that would indicate any substantial deviation from true mirror symmetry through the molecule. Hence our assumption of the centrosymmetric space group was substantiated.

The weighting scheme gave values of $\Sigma w[|F_o| - |F_c|]^2$ which did not differ by $>50\%$ for different ranges of $|F_o|$ and sin θ, thereby satisfying a criterion set by Cruickshank.[11] The final standard deviation of an observation of unit weight was 1·54, indicating an underestimation of the standard deviations of the intensity data.

The data collection programs for the PDP 8/e and the other programs for the IBM 370/155 computer used in this structure analysis and interpretation are those listed previously.[4]

RESULTS

Observed and final calculated structure factors are listed in Supplementary Publication No. SUP 20551 (3 pp., 1 microfiche).* The molecular structure and atom number-

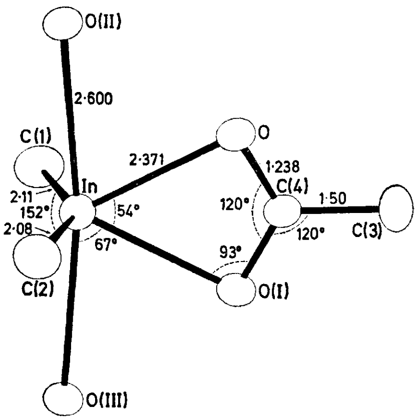

FIGURE 1

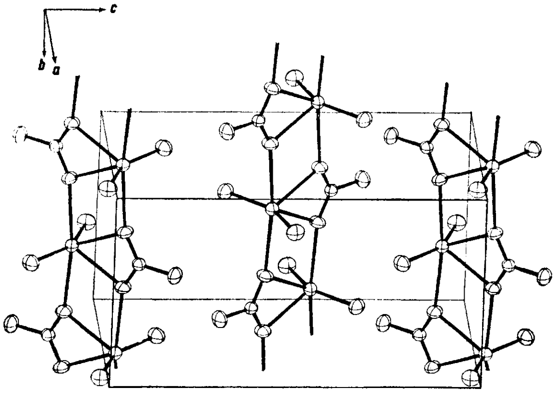

FIGURE 2

TABLE 1

Fractional atomic co-ordinates and thermal parameters (Å^2) * with standard deviations in parentheses

Atom	x	y	z
In	0·07530(9)	0·25	0·05970(5)
O	−0·0871(7)	0·1040(6)	−0·0727(4)
C(1)	−0·1219(18)	0·25	0·1762(10)
C(2)	0·3459(18)	0·25	0·0075(11)
C(3)	−0·2668(17)	0·25	−0·1992(9)
C(4)	−0·1405(14)	0·25	−0·1095(8)

* Anisotropic temperature parameters in the form: $\exp[-2\pi(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$:

	U_{11}	U_{22}	U_{33}
In	0·0694(6)	0·0577(5)	0·0558(5)
O	0·097(4)	0·044(3)	0·084(3)
C(1)	0·104(9)	0·068(7)	0·089(8)
C(2)	0·076(7)	0·087(9)	0·103(9)
C(3)	0·089(8)	0·088(8)	0·074(7)
C(4)	0·063(6)	0·041(6)	0·054(5)

	U_{12}	U_{13}	U_{23}
In	0	−0·0029(5)	0
O	0·001(2)	−0·018(3)	0·004(2)
C(1)	0	0·023(8)	0
C(2)	0	0·005(8)	0
C(3)	0	−0·014(7)	0
C(4)	0	0·002(5)	0

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[11] D. W. J. Cruickshank in ' Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon Press, Oxford, 1965, p. 113.

ing scheme are shown in Figure 1. A view of the unit cell illustrating the packing of the molecules in chains is shown in Figure 2. Final atomic positions and thermal parameters are given in Table 1 with the least-squares estimated standard deviations. Inter- and intra-molecular distances and bond angles are given in Table 2; errors in these distances and angles include contributions from the variance–covariance matrix and errors in all dimensions. The equations for (least-squares) planes through selected atom-groups and the distances of pertinent atoms from these planes are given in Table 3.

TABLE 2

Distances and angles

	$Me_2(CH_3CO_2)In$	$(Et_2CH_3CO_2)In$ *	$Et_2(CH_3COS)In$ *
(*a*) Distances (Å)			
In–C(1)	2·11(1)	2·29	2·14
In–C(2)	2·08(1)	2·22	2·14
In–O	2·371(5)	2·46	2·56
In–O^{II}	2·600(5)	2·64	2·47
C(4)–O	1·238(7)	1·24	1·27
C(4)–C(3)	1·50(1)	n.g.	1·47
(*b*) Angles (°)			
C(1)–In–C(2)	152·2(6)	126	
O^{II}–In–O^{III}	171·5(2)		
O–In–O^{II}	67·4(2)		
O–In–O^{I}	53·6(2)		
In–O–In^{II}	112·6(2)	111	
In–O–C(4)	93·4(5)	93·5	99
C(3)–C(4)–O	120·3(5)	119·5	121
O–C(4)–O^{I}	119·4(9)	121	

Roman numerals as superscripts refer to the following symmetry transformations:

I $x, \frac{1}{2} - y, z$ III $-x, \frac{1}{2} + y, -z$
II $-x, -y, -z$

* Values for the standard errors were not quoted. In both cases, values were taken from figures and some of the distances and angles were not given or, in the case of the thioacetate compound, not applicable.

DISCUSSION

The crystal structure consists of six-co-ordinate indium atoms, with the indium surrounded by two methyl groups and a bidentate acetate group as well as being co-ordinated to the acetate groups of the two neighbouring molecules. The molecules are therefore linked into chains giving rise to a polymeric type lattice (Figure 2). While there are examples of the carboxylate group acting as an *anti–anti* or *syn–anti* bridges between metal atoms and other examples of the groups acting as a bidentate ligand forming a four-membered ring,[12] the acetate group in the present compound is acting as both types of ligand simultaneously. This type of association has been reported for relatively few compounds, namely $Ca[(AcO)_4M],6H_2O$ (M = Cu and Cd [13]), uranium(IV) acetate,[14] and $(AcO)_2Cd,2H_2O$.[15] In all of these cases the M–O(bridging) bond is the same length or shorter than the M–O(chelating) bond; this situation is very different from that found in indium acetates and will be discussed.

As can be seen from Table 3, the acetate group is very nearly a perfect plane. While this group is tilted with respect to the InO_2 plane by a crystallographically significant amount, 2·6(5)°, there is nothing of chemical importance in this fact and it is probably a slight distortion due to crystal packing forces. The most remarkable feature of the acetate group is its lack of distortion, *i.e.* all bond distances and angles having values so close to those expected for an isolated acetate ion.

TABLE 3

Equations of best weighted least-squares planes in the form $Ax + By + Cz + D = 0$; * distances (Å) of atoms from the planes are given in square brackets

	A	*B*	*C*	*D*	χ^2 †
Plane (1):					
O, O^{I}, C(3), C(4)	0·789	0	−0·614	−0·093	0·3
[O 0·0005, O^{I} 0·0005, C(3) 0·002, C(4) −0·005, In −0·148]					
Plane (2):					
In, O, O^{I}, O^{II}, O^{III}	0·831	0	−0·557	−0·013	47·0
[In 0·001, O −0·002, O^{I} −0·002, O^{II} −0·024, O^{III} −0·024]					
Plane (3):					
In, On^{II}, O, C(4)	0·826	0·003	−0·564	−0·011	22·2
[In 0·000, In^{II} 0·000, O 0·018, C(4) −0·030]					

* Equations, expressed in Å, refer to axes *x*, *y*, *z*, parallel to *a*, *b*, *c*, respectively. † $\chi^2 = \sum_{i=1}^{N} [P_i^2/\sigma^2(P_i)]$ where *N* is the number of atoms in the plane and $\sigma^2(P_i) = A\sigma^2(x_i) + B\sigma^2(y_i) + C\sigma^2(z_i)$. $\sigma(x_i)$ is the estimated standard deviation in the *x* direction of atom *i* and P_i is the distance of the atom from the plane.

The structural similarities between the free acetate anion and ligand acetate in $Me_2(AcO)In$ confirms the conclusion reached from studies of the vibration spectra, reported elsewhere. This is somewhat surprising, despite the rather long In–O bond, since some changes in the bond order might have been expected on complex formation. A possible explanation is that in the acetate anion, the oxygen atom bonding in the C–O bond is conventionally described in terms of an sp_x oxygen orbital, which is σ bonding, a p_z π orbital, and a non-bonding (occupied) p_y orbital. For a bridging acetate ligand, as in the present case, the oxygen is more readily seen to be in an sp^2 hybrid state: the three lobes interact with the acetate carbon, and two indium atoms, with the remaining p_π orbital also interacting with a similar carbon orbital. This retains the bond order of $1\frac{1}{2}$ in the C–O bond in both anion and ligand, and emphasizes that a bidentate bridging stereochemistry need not change the C–O bond order.

The structure of acetatodimethylindium(III) is very

---

[12] C. Oldham, *Progr. Inorg. Chem.*, 1968, **10**, 225, and references therein.

[13] D. A. Langs and C. R. Hare, *Chem. Comm.*, 1967, 890.

[14] I. Jelenic, D. Grdenic, and A. Bezjak, *Acta Cryst.*, 1964, **17**, 758.

[15] W. Harrison and J. Trotter, *J.C.S. Dalton*, 1972, 956.

similar to that reported for acetatodiethylindium(III)[9] and similar in many ways to that of diethyl(thioacetato)-indium(III).[8] The quoted distances and angles for the two diethyl compounds are given in Table 2 for comparison with the present structure. Those distances and angles which were not given for the $Et_2(AcO)In^{III}$, appear to have values close to the corresponding ones in $Me_2(AcO)In^{III}$. The only major difference that is obvious between the ethyl and methyl structures is that the In–C and In–O bond lengths in the former all appear to be longer and the C–In–C angle is much smaller; however since no standard deviations are given for these values, no assessment can be made as to the significance of these differences.

In the thioacetate structure, this group, like the acetate in the present structure, acts as a bidentate ligand, forming a four-membered ring consisting of In–O–C–S and also as a bridging ligand, with the oxygen bridging two indium atoms. Although the packing would seem to favour such an arrangement, the sulphur atom does not take part in a bridge formation as does the corresponding oxygen in both acetate compounds; instead it only participates as part of the bidentate ligand. The result of this is to reduce the co-ordination of indium from six in the acetate to five in the thioacetate compound. In the two acetate compounds the two indium–oxygen bonds differ by $>0{\cdot}2$ Å, with the bidentate oxygen bond the shorter, while in the thioacetate the two indium–oxygen bonds differ by $<0{\cdot}1$ Å, and the bridging bond is then the short one. In all three of these compounds, the In–O bond lengths (2·37—2·64 Å) are much longer than those found in other oxygen-co-ordinated indium compounds [2·15—2·20 in $InI_3,(Me_2SO)_2$[16] and 2·23 Å in $(NH_4)_2InCl_5,H_2O$[17]].

The similarity of the acetate and thioacetate compounds is certainly reflected in the packing of the molecules and in the space group of the two compounds. There is an interchange in the *b* and *c* axis between the two compounds. In the acetate compounds the mirror plane perpendicular to the *b* axis is also perpendicular to the plane of the acetate and the two methyl (ethyl) groups on the indium are independent of each other and lie in the mirror plane. The situation is reversed in the case of the thioacetate, where the thioacetate group as a whole lies in the mirror plane and the ethyl groups are symmetry-related across the mirror, just as the oxygen atoms are in the acetate compounds. Except for this change of axis, the cell dimensions for the three compounds differ only by the amounts which might be expected.

The structure of crystalline $Me_2(AcO)In$ once again demonstrates the tendency of indium(III) to increase its co-ordination where possible.

A monomeric structure obviously requires four-co-ordinate indium (InC_2O_2) which is ' co-ordinatively unsaturated.' This tendency to interact in some way to remove such unsaturation has been demonstrated in many previous studies, and in particular it has been shown that the co-ordination number readily increases to six when small electronegative, σ donor atoms are involved. The present result is clearly in keeping with these earlier conclusions. A study of the gas-phase structure of $Me_2(AcO)In$ should be instructive, as would be a study of its interactions with neutral donor-ligands.

[2/1917 *Received*, 14*th August*, 1972]

---

[16] F. W. B. Einstein and D. G. Tuck, *Chem. Comm.*, 1970, 1182.

[17] H. P. Klug, E. Kummer, and L. A. Alexander, *J. Amer. Chem. Soc.*, 1948, **70**, 3064.