Co-ordination Compounds of Indium. Part XXI.[1] Some Compounds Derived from Indium(III) Acetate, including Indium Diacetate

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Electrolysis of indium in acetic acid produces fine metallic crystals, which when set aside are converted into $In(OAc)_2$. This compound has been compared with $In(OAc)_3$, $In(HCO_2)_3$, and $(Me)_2In(OAc)$, all of which appear to have polymeric carboxylate-bridged lattices. The pyridine adduct of $In(OAc)_3$, and the new compounds $(Me_4N)_3In(OAc)_3(ClO_4)_3$ and $(Et_4N)_3In(OAc)_6$, involve insertion of the appropriate species into the polymeric lattice of $In(OAc)_3$. The structure of $In(OAc)_2$ is believed to be a lattice of $In(OAc)_3$ + In^IOAc, similar to the other compounds, but unrelated to the indium ' dihalides '.

WE are currently investigating compounds in which indium is in an oxidation state lower than (III). The earlier work in this field is reviewed elsewhere.[2,3] The present work arose from studies on compounds in which indium forms complexes with carboxylate anions.

In the kinetic studies of the reducing action of indium(I) species, Sykes and his co-workers [4,5] showed that aqueous solutions of indium(I) can be prepared by electrolytic oxidation of the metal. We have therefore investigated the use of electrolysis for the direct preparation of compounds of the lower oxidation states of indium, especially in non-aqueous solvents. We find that with almost anhydrous acetic acid, electrolysis initially produces a deposit of fine crystals of indium metal, which when set aside are converted into colourless crystals of $In(OAc)_2$, a hitherto unknown member of the group of compounds of stoicheiometry InX_2, whose structures have been the subject of much discussion.[3]

We have also examined indium(III) acetate [6] and formate,[7] and have attempted to obtain adducts of these compounds with a variety of donor ligands. Electrolysis of indium in almost anhydrous formic acid produces indium metal, but extended contact with the electrolyte converts this into indium(III) formate. Both indium(III) acetate and formate are found to be much weaker acceptors than the halides [8] or pseudo-halides [9,10] of indium(III).

Indium Acetates.—Indium metal is not attacked by anhydrous acetic acid at a detectable rate, even when heated under reflux, and the simplest route to indium(III) acetate therefore involves dissolving the hydroxide and crystallising.[6] Similar procedures apply for indium(III) formate. In contrast to the resistance of the bulk metal to attack by acetic acid, the freshly deposited crystals obtained electrolytically are slowly converted by the acid into a colourless diamagnetic crystalline substance, of stoicheiometry $In(OAc)_2$. The metallic crystals are long and acicular: micrographs showed that the reaction proceeds by surface attack, and specimens of metal surrounded by colourless material could be isolated from the solid.

Despite the apparent homogeneity of the final material, detailed examination showed that each ' crystal ' in fact consisted of a mass of very fine needle-like crystallites. An *X*-ray oscillation photograph showed ' a pattern characteristic of a bundle of crystalline fibres (*e.g.* nylon), with a repeat distance of 3·6 Å (1 Å = 10^{-10}M).' Indium diacetate is readily converted into $In(OAc)_3$ by heating under reflux in acetic acid.

Mass-spectrometric Studies.—Neither $In(OAc)_2$ nor $In(AOc)_3$ is sensibly volatile, but the mass spectra of solid sources reveal that a number of ions can be obtained; many of these clearly originate in the acetate ion, or its decomposition products, but the indium-containing species are readily identified from the characteristic $^{113}In + ^{115}In$ pair. The main peaks, in order of decreasing intensity, are at the following m/e values (for the ^{115}In species): $In(OAc)_3$ (250 °C), 233, 115, 191, 174, and 159; $In(OAc)_2$ (300 °C), 233 and 115. The mass spectrum of the diacetate, even at a source temperature of 300 °C, was of very low intensity. The peaks at m/e 233, 174, and 191 correspond to $In(OAc)_2^+$, $In(OAc)^+$, and $In(OAc)(OH)^+$ respectively (all for ^{115}In). The predominance of InX_2^+ species has also been observed in the mass spectra of indium halides, and has been related to the fact that such ions are isoelectronic with the thermodynamically stable neutral CdX_2 compounds.[11] The absence of a parent peak from $In(OAc)_3$, and the involatility of this substance, provide some evidence that this compound should not be formulated as a monomer with three chelating acetate ligands; for example, while the most abundant ion in the mass spectra of tris(diketonato)indium(III) compounds under similar conditions is $In(L)_2^+$, there is a significant molecular-ion peak.

We have also recorded the mass spectrum of dimethylacetatoindium(III), first prepared by Clark and Pickard.[12] At 80 V, and an inlet temperature of 90 °C,

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[1] Part XX, A. F. Berniaz and D. G. Tuck, *J. Organometallic Chem.*, 1972, **46**, 243.

[2] G. Contreras and D. G. Tuck, *Chem. Comm.*, 1971, 1552.

[3] G. Contreras, J. S. Poland, and D. G. Tuck, *J.C.S. Dalton*, in the press.

[4] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1969, 2419.

[5] R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1628.

[6] ' Handbuch der Anorganischen Chemie,' vol. 37, Gmelin, 1936, p. 107.

[7] Ref. 6, p. 108.

[8] A. J. Carty and D. G. Tuck, *J. Chem. Soc.* (*A*), 1966, 1081.

[9] S. J. Patel, D. B. Sowerby, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1967, 1187.

[10] S. J. Patel and D. G. Tuck, *J. Chem. Soc.* (*A*), 1968, 1870.

[11] P. Dobud and D. G. Tuck, unpublished results.

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

the predominant peaks at $m/e > 115$ are 145 ($InMe_2^+$), 130 ($InMe^+$), and 189 [$MeIn(OAc)^+$], with smaller contributions at 233, 174, and 204 (molecular ion). Significantly, there are also ions at 393 [$Me_3In_2(OAc)_2^+$] and 319 [$Me_2In_2(OAc)^+$], with a series of lower intensity peaks representing masses between these and the monomeric species below m/e 204, indicating the existence of dimeric species in the gas phase of Me_2InOAc (see later).

Thermogravimetric Decomposition Studies.—The thermal decomposition patterns of $In(OAc)_2$ and $In(OAc)_3$ in air were investigated by use of a standard thermogravimetric balance. The two compounds show similar behaviour. With $In(OAc)_3$, the first sharp decomposition at 350 °C corresponds to the loss of two acetate groups per indium followed by the loss of H_2O at 400 °C. A gradual loss of weight over the range 400—1000 °C is followed by a more pronounced change between 1000 and 1100 °C, at which temperature the weight of the residue demonstrates complete conversion into In_2O_3 (Found: In 82·6; Calc. for In_2O_3: In, 82·7%). The nature of these high-temperature changes was not investigated further.

With $In(OAc)_2$ under identical conditions the first step in the thermogram is again a pronounced change beginning at 325 °C, and corresponding in this case to the loss of one acetate per indium. The loss of water, the gradual change up to 1000 °C, and the ultimate formation of In_2O_3 (Found: In, 82·6%) are all very similar to the changes in the tri-acetate case, and occur at similar temperatures.

No attempt was made to identify the intermediate species produced in these thermal decompositions. The results do serve to establish the close similarity in the thermal stabilities of the two indium acetate compounds. We suggest that $In(OAc)_2$ can be regarded as a lattice complex of $In(OAc)_3 + In(OAc)$, so that the decomposition in the presence of oxygen must involve an oxidation of the latter, probably to $In(OAc)O$, with subsequent decomposition to In_2O_3, together with those processes characteristic of the oxidative degradation of $In(OAc)_3$.

Adducts of Indium Acetates.—The ready formation of addition compounds with donor ligands is a characteristic feature of the chemistry of the indium(III) halides and pseudohalides. In contrast, indium(III) triacetate is an extremely weak acceptor, and the only 1 : 1 adduct we were able to obtain was $In(OAc)_3$,py (py = pyridine). Similar results were found with indium(III) formate, but in both cases, the adducts are unstable, losing pyridine slowly at room temperature. No stoicheiometric adducts could be obtained with indium diacetate; there was some indication of reaction with pyridine, but the product formed was very unstable with respect to loss of pyridine, and of irreproducible composition.

The weak acceptor property of indium(III) acetate and formate is clearly in part a result of the high basicity of the anions. An additional factor is related to the structure of the parent compounds, which are believed to exist as a polymeric lattice with bridging carboxylate groups (see later). The co-ordination of a further molecule to indium, as in the formation of an adduct, must then require either that this donor molecule can be accommodated into the lattice, or that the lattice be disrupted into monomeric units in the addition reaction. Either of these processes will require energy over and above that involved in the formation of the indium–donor co-ordinate-bond, perhaps considerably so in the latter case.

The ready reversibility of the addition process with pyridine suggests that co-ordination is to an indium atom which continues to be part of a polymeric lattice, which is able to accommodate the extra molecule of donor. Ethylenediamine (en) apparently represents the alternative route, that of completely disrupting the lattice, giving a product, formulated as $[In(en)_3]^{3+}(OAc^-)_3$, which is stable up to its melting point (200 °C). Salts of this cation have been reported previously with perchlorate [13] and nitrate,[14] and the present compound has similar solubilities, *etc*., to these species.

The unusual $(Et_4N)_3In(OAc)_3(ClO_4)_3$ contains ionic perchlorate, and is therefore seen as a lattice compound in which the polymeric indium(III) acetate lattice now incorporates Et_4N^+ and ClO_4^- ions. The compound $(Me_4N)_3In(OAc)_6$ may well have a similar type of structure. We attempted to resolve this question by measurements of the molar conductivities in nitrobenzene. Even at mM concentrations, such solutions are unstable, throwing down a precipitate after 5—10 min, so that the results refer to measurements made 2 min after preparation of the solution. Under these conditions, the molar conductivities (ohm^{-1} cm^2) are: $In(OAc)_3$,py 38, $[In(en)_3](OAc)_3$ 116, $(Me_4N)_3In(OAc)_6$ 290, and $(Et_4N)_3In(OAc)_3(ClO_4)_2$ 297. In view of the instability of the solutions, a quantitative discussion is unjustified, but the order of conductivities,[15] and the similarities in the last two results, is in keeping with the structures suggested for these adducts.

Vibrational Spectra.—The vibrational spectra of the acetate and formate anion have been studied in detail,[16] and we refer to these results throughout the subsequent discussion. The ν(In–O) modes are expected to occur below *ca*. 450 cm^{-1}; formate has no vibrations in this region, and acetate only a weak i.r. absorption [16] at 460 cm^{-1}. The Raman emission from aqueous solutions of indium(III) oxyanion salts (350—460 cm^{-1}) has been assigned [17] to the totally symmetric $M \leftarrow (OH_2)_n$ breathing mode. Similarly, lines at 433 and 444 cm^{-1} in the Raman spectrum of tris(acetylacetonato)indium(III) are believed to arise from vibrations in which ν(In–O) is a major component.[18]

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[13] A. J. Carty and D. G. Tuck, *J. Chem. Soc.*, 1964, 6012.

[14] D. G. Tuck, E. J. Woodhouse, and P. Carty, *J. Chem. Soc.* (*A*), 1966, 1077.

[15] D. M. Murray-Rust, J. J. Hadow, and Sir Harold Hartley, *J. Chem. Soc.*, 1931, 215.

[16] K. Ito and H. J. Bernstein, *Canad. J. Chem.*, 1956, **34**, 170.

[17] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 768.

[18] R. E. Hester and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 513.

We first discuss the vibrational modes of dimethylacetatoindium, the crystal structure of which has been studied by *X*-ray methods.[19] This compound gives rise to a polymeric lattice in which acetate groups bonded to one Me_2In moiety also bridge to two other $Me_2In(OAc)$ units. Each acetate oxygen is therefore three-co-ordinate (2 In, 1 C), and each indium six-co-ordinate, forming two $In{-}CH_3$ bonds, two short $In{-}O^{I}$ bonds (2·37 Å) to a single acetate, and two long $In{-}O^{II}$ bonds (2·60 Å) to each of two other acetates. Table 1 lists part of the vibrational spectrum of solid dimethylindium(III) acetate in the region 750—250 cm^{-1} (i.r.) and 750—150 cm^{-1} (Raman). The Raman spectra of all the compounds examined were of poor quality <*ca.* 400 cm^{-1}. The $\nu(In{-}CH_3)$ and $In{-}CH_3$ rocking modes are readily identified by comparison with recent studies of other such species,[20,21] and are in good agreement with earlier i.r. results.[12] The local symmetry of the $Me_2In(O^{I})_2(O^{II})_2$ unit in the crystal is C_{2v}, which requires two $\nu(In{-}CH_3)$, both i.r.- and Raman-active, and the bands at 554 and 496 are therefore readily assigned as ν_{as} and ν_{sym} $(In{-}CH_3)$.

TABLE 1

Vibrational spectrum (cm^{-1}) * of dimethylacetatoindium(III)

I.r.	R	
728s,br		$In{-}CH_3$ rock
554s	551vw	$\nu_{as}(In{-}CH_3)$
497mw	496vs	$\nu_{sym}(In{-}CH_3)$
	375w	
320sh	325w	$\nu(In{-}O)$
298m		
	225mw	$\delta(In{-}O)$
	190w	

* See also Table 2; s = strong, m = medium, w = weak, br = broad, sh = shoulder.

A discussion of the $\nu(In{-}O)$ modes is more difficult, since any discussion based on the local symmetry ignores the extensive coupling which must occur between the $\nu(In{-}O^{I})$ and $\nu(In{-}O^{II})$ vibrations. We therefore identify the bands between 375 and 298 cm^{-1} as $\nu(In{-}O)$, with the $\delta(In{-}O)$ modes lying <250 cm^{-1}. Precise assignments have not been attempted in view of the poor quality of the Raman spectra, but these identifications prove important in the following discussions.

TABLE 2

$\nu(CO)$, $\nu(CC)$, and (In–O) vibrations (cm^{-1}) in acetate anion, indium(III) acetate, and some related compounds

OAc^- [a]	$In(OAc)_3$	$In(OAc)_2$	$Me_2In(OAc)$	$(Me_4N)_3In(OAc)_6$	$(Et_4N)_3In(OAc)_3(ClO_4)_3$
ν_8, $\nu(CO)$ 1578s (i.r.)	1540vs (i.r.)	1548vs (i.r.)	1530s,br (i.r.)	1592s,br (i.r.)	1556vs,br (i.r.)
ν_3, $\nu(CO)$, 1413s (i.r., R)	1422s (R)	1426 (R) 1420 (i.r.)	1445s,br (i.r.) 1420 (R)	1448m (i.r.) 1462 (R)	1447s,br (i.r.) 1451m (R)
ν_4, $\nu(CC)$, 926s (R)	955s (R) 950w (i.r.)	954s (R)	956s (i.r.) 966w (R)	960s (i.r.) 957m (R)	
In–O R	376w, 283m, 225mw	368w, 282w, 225w	*b*	374w, 350w, 267w	391m, 348w, 265w, 224w
In–O i.r.	350sh, 325m, 290w, 250sh, 230s	355sh, 330m, 283w, 250sh, 225s	*b*	350w, 315m,br, 280sh, *ca.* 230s,br	320m,br, 280w, *ca.* 230s,br

[a] Results and assignments for Na(OAc) from ref. 16. [b] See Table 1.

Table 2 gives results for those regions of the vibrational spectra of $Me_2In(OAc)$, $In(OAc)_3$, $In(OAc)_2$ and related compounds which show significant changes from the vibrations of the acetate ion.[16] The limitations in the use of vibrational spectroscopy in identifying the mode of co-ordination of the acetate ligand (*i.e.* uni- or bidentate, or bridging) have been emphasised,[22] and the only immediate conclusions to be drawn from the present results are that none of the compounds involves unidentate acetate, and that the acetate is apparently in a similar environment in all these indium species, with a slight decrease in the $\nu(CO)$ force-constant and a similar increase in $\nu(CC)$ relative to the free acetate anion. This result is in keeping with the *X*-ray structural results [19] for $Me_2In(OAc)$, in which the bond lengths and angles of the acetate ligand are close to those in anionic acetate.

The vibrations in the $\nu(In{-}O)$ region, and below, identified by comparison with the spectrum of $Me_2In(OAc)$, are also reasonably constant for all the compounds listed in Table 2. The physical properties of indium(III) acetate are not those of a simple mononuclear trischelate, and we suggest that both physical and chemical properties are best interpreted in terms of a carboxylate-bridged linear polymer, similar to that found in $Me_2In(OAc)$. In the light of the discussion of the $\nu(In{-}O)$ spectrum of that compound, the spectra cannot be used to identify the local symmetry of the $In{-}O_6$ kernel. The similarities in the spectra listed in Table 2 in both the ligand vibrations and the $\nu(In{-}O)$ region support the view that the indium(III) acetate structure is retained in $(Me_3N)_3In(OAc)_6$, $(Et_4N)_3In(OAc)_3(ClO_4)_3$, and $In(OAc)_2$.

In addition to the bands listed in Table 2, the spectrum of $(Me_4N)_3In(OAc)_3(ClO_4)_3$ shows vibrations at 933vs (R), 458m (R), *ca.* 1090vs (i.r.) + 1072m (R), and 625m (i.r.) + 626m (R), indicating the presence of ionic perchlorate (ν_1—ν_4 respectively). There is some slight uncertainty in the value for ν_3 in the i.r. because of incompletely resolved overlapping bands of the acetate group. There is no evidence for any bonding of perchlorate to indium, so that the solid must consist of the

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[19] F. W. B. Einstein, M. M. Gilbert, and D. G. Tuck, following paper.

[20] C. W. Hobbs and R. S. Tobias, *Inorg. Chem.*, 1970, **9**, 1998.

[21] J. S. Poland and D. G. Tuck, *J. Organometallic Chem.*, 1972, **42**, 315.

[22] For example, I. R. Beattie and T. Gibson, *J. Chem. Soc.*, 1961, 2585.

original polymeric indium(III) acetate array, with three tetramethylammonium cations and three perchlorate anions incorporated into the lattice. A similar structure is suggested for $(Et_4N)_3In(OAc)_6$, by slightly different arguments. A mononuclear anion $[In(OAc)_6]^{3-}$ would require either six bidentate acetate groups with twelve-co-ordinate indium, which is most unlikely, or six unidentate acetate groups, in which case one should observe ν(C=O) in the i.r. spectrum. Typical frequencies[18,19] for this vibration are 1700—1775 cm^{-1}. No i.r. absorption was detected in this region, and we therefore conclude that the solid is effectively $In(OAc)_3$ polymer + $3Et_4N^+$ + $3(OAc^-)$. The similarities in the spectra of ionic and bridging acetate do not allow separate identification of the separate sets of vibrations to be expected from such a structure.

The low-frequency vibrational spectrum of the ethylenediamine compound $In(OAc)_3(en)_3$ is apparently unrelated to those of the other adducts. The pattern in the i.r. region is: 455m, 380, 350, 315, and 280 cm^{-1} (all w); and in the Raman 470, 397, 362, 308, 220, and 175 cm^{-1} (all w), which is completely different from the spectra in this region in Table 2. The bands at 455 and 470 cm^{-1} are stronger than the weak COO rocking mode in anionic or ligand acetate (*cf.* ref. 16). The bands in the 350—470 cm^{-1} region are probably ν(In–N) modes, since ν(Zn–N) in $[Zn(en)_3]^{2+}$ has been identified[24] as 425 cm^{-1}. The spectra are in agreement with the formulation of the compounds as $[In(en)_3](OAc)_3$.

The probable structure of the pyridine adduct was discussed earlier. The vibrational spectrum of this compound is too complex for analysis, but we note that slight increases in the frequency of bands 4 (768 cm^{-1}) and 16 (430 cm^{-1}) (using the notation in the compilation by Adams,[25] following Kline and Turkevitch[26]) are very close to those reported for co-ordinated pyridine.

TABLE 3

Vibrational spectra (cm^{-1}) of the formate anion, and of indium(III) formate

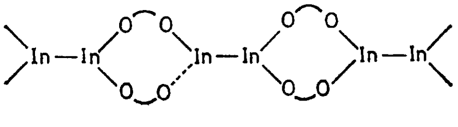
	HCO_2^-		$In(HCO_2)_3$	
Assignment	R	I.r.[a]	R	I.r.
ν_1	2803	2841	2942w, 2906s, 2870w	2920w
ν_2	1349	1366	1370sh	1365s,br
ν_3	762	772	800w,br	795s
ν_4		1567		1565s,br
ν_5	1380	1377	1388s	1385sh
ν_6	1066	1073	1036w	
			388s	371m
			348m	348m
			256w	310sh
			181w	288m
			105w	

[a] Data for solid $Na(HCO_2)$ from ref. 15.

Table 3 presents a comparison of our results for $In(HCO_2)_3$ with those reported[16] for sodium formate. The changes in the spectrum of the ligand are slight, and the number of bands reasonably assigned to ν(In–O) is analogous to that in the case of $In(OAc)_3$. We therefore conclude that the structure of indium(III) formate is similar to that of indium(III) acetate on the basis of these results.

Nature of Indium Diacetate.—The structure of the indium dihalides, and in particular of indium dichloride and related species, has been the subject of much discussion. The two structures most strongly urged involve either a metal–metal bonded dimer $X_2M–MX_2$, or an ionic dimer of mixed oxidation state $M^I[M^{III}X_4]$. This latter is generally accepted for the gallium dihalides, and evidence supporting this structure for indium dibromide and di-iodide has recently been obtained.[3]

For indium diacetate, the mass spectrum shows no evidence of ions derived from $(OAc)_2In–In(OAc)_2$. The vibrational spectrum equally provides no evidence for this structure, which would give a different ν(In–O) spectrum from the six-co-ordinate $In(OAc)_3$ species, whereas the spectra of $In(OAc)_2$ and $In(OAc)_3$ are very similar in all respects, and this structure can therefore be rejected. A polymeric lattice can be rejected by similar reasoning. The structure $In^I[In(OAc)_4]$, by analogy with the bromide and iodide, would require either four- or eight-co-ordinate indium in the anion, but again no evidence for this was obtained.



Examination of the spectroscopic, physical, and chemical properties of this material, together with the *X*-ray evidence, forces us to conclude that indium diacetate is, like the other compounds discussed, a polymeric $In(OAc)_3$ lattice incorporating equimolar quantities of indium(I) acetate. The nature of this latter species, and of the interactions between this and the host lattice, are at present unclear, and further experiments on this aspect of the problem are planned. It is however clear that there is little in common between $In(OAc)_2$ and the Group III dihalides.

EXPERIMENTAL

General.—Materials, and spectroscopic techniques, were as described previously. In the electrolytic experiments, power units supplying up to 0·5 A (D.C.) at 40 V (*e.g.* Power Designs 4005) were used.

Indium analysis was carried out by atomic absorption spectroscopy, by use of a Perkin-Elmer 305 instrument. Total acetate was determined in some cases by distilling acetic acid, released by treatment with sulphuric acid, into standardised aqueous caustic soda solution.

Magnetic susceptibilities were measured on a con-

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[23] L. A. Duncanson, W. Gerrard, M. F. Lappert, H. Pyszora, and R. Shafferman, *J. Chem. Soc.*, 1958, 3652.

[24] G. R. Cayley and D. N. Hague, *Trans. Faraday Soc.*, 1971, **67**, 2896.

[25] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967, pp. 278, 306.

[26] C. H. Kline and J. Turkevitch, *J. Chem. Phys.*, 1944, **12**, 300.

ventional Faraday balance, previously calibrated against $HgCo(CNS)_4$.

Preparation of Indium Di- and Tri-acetates.—Indium(III) acetate was obtained by dissolving washed indium(III) hydroxide in the minimum volume of hot (70 °C) concentrated acetic acid. Evaporation produced white crystals of indium(III) acetate, m.p. 280 °C (decomp.) [Found: In 39·3, acetate 60·7; $In(OAc)_3$ requires In 39·4, acetate, 60·6%]; μ_{eff} $-71·9 \times 10^{-6}$ c.g.s. units.

In the electrolytic experiments, the anode consisted of *ca.* 1 g indium shot, beaten onto a platinum wire to form a plate *ca.* 2 cm^2 in area, and the cathode was *ca.* 2·5 cm^2 of platinum sheet. Pure acetic acid is a very poor electrical conductor, but the addition of small amounts of water allows sufficient current to flow; the electrolyte finally used was glacial acetic acid (75 ml) plus water (5 ml). The best results were obtained by working at 10 V and 10 μA. After *ca.* 5 h, finely divided feathery crystals of indium metal had formed on the cathode; after further electrolysis, or prolonged contact with the electrolyte liquor, these were transformed into colourless crystals of $In(OAc)_2$, m.p. 265 °C (decomp.), and μ_{eff} $-81·8 \times 10^{-6}$ c.g.s. units (Found: C, 19·8; H, 2·7; In, 49·2; OAc^-, 50·4. $C_4H_6InO_4$ requires C, 20·5; H, 2·6; In, 49·3; OAc^-, 50·5%).

Heating $In(OAc)_2$ under reflux in glacial acetic acid for 3 h gave a clear solution, from which indium tri-acetate was recovered on removal of excess acetic acid.

Indium(III) *Triacetate–Pyridine.*—Indium triacetate was added in 0·5 g portions to pyridine heated under reflux over a period of 24 h, more solid being added whenever the solution was clear. Addition of light petroleum to the cooled solution produced a precipitate of the *product*, which was washed and dried under nitrogen (Found: C, 35·1; H, 3·6; In, 30·4; N, 4·0. $C_6H_9InO_6,C_5H_5N$ requires C, 35·6; H, 3·8; In, 30·9; N, 3·8). This compound is air sensitive, releasing pyridine on exposure to the atmosphere.

Tris(*ethylenediamine*)*indium*(III) *Triacetate.*—Indium triacetate was dissolved in ethylenediamine at 40 °C; the white crystals which were precipitated on cooling were washed with ether and recrystallized from ethanol (Found: C, 30·0; H, 6·9; In, 24·3; N, 18·0. $C_{12}H_{33}InN_6O_6$ requires C, 30·5; H, 7·0; In, 24·3; N, 17·8%).

$(Me_4N)_3In(OAc)_6$.—Tetramethylammonium hydroxide in water was neutralized with concentrated aqueous acetic acid, and the solution evaporated to dryness. The resultant solid was recrystallised from ethanol, and treated with a three-fold excess of $In(OAc)_3$ suspended in water. After shaking for 20 min, the suspended solid dissolved, and the solution was then evaporated to dryness to yield a hygroscopic *solid* $(Me_4N)_3In(OAc)_6$, which was recrystallised from ethanol and dried *in vacuo* (Found: C, 41·8; H, 7·8; In, 16·5; N, 6·1. $C_{18}H_{15}InN_3O_6$ requires C, 41·7; H, 7·8; In, 16·7; N, 6·1%]. In a related experiment, indium(III) acetate was added to an aqueous ethanolic solution of tetraethylammonium perchlorate, and the mixture heated under reflux for 30 min. Excess of solid was then filtered off, and light petroleum ether added to the filtrate; the white *crystals* which precipitated were recrystallised from ethanol and dried *in vacuo*. This substance, $(Et_4N)_3In(OAc)_3(ClO_4)_3$, m.p. 265 °C (decomp.) is extremely hygroscopic [Found: C, 36·2; H, 7·2; In, 11·6; N, 4·2. $C_{14}H_{29}Cl_3InN_3O_{10}$ requires C, 36·8; H, 7·0; In, 11·7; N, 4·3%]. The same compound was obtained from reaction mixtures containing excess of tetraethylammonium perchlorate.

Indium(III) *Formate.*—Indium(III) hydroxide was dissolved in formic acid at 50 °C, and the solvent evaporated to give white indium(III) formate [Found: C, 15·0; H, 1·3; In, 45·1. Calc. for $C_3H_3InO_6$: C, 14·4; H, 1·2; In, 45·0%]. Electrolysis of indium in dried formic acid under conditions similar to those used in the acetic acid experiments produced indium metal, which when set aside was converted into white crystals of indium(III) formate [Found: C, 14·2; H, 1·3; In, 45·0%]. Only with pyridine was there any evidence of formation of an adduct: heating under reflux with this solvent gave *indium*(III) *triformate–pyridine* [Found: C, 28·7; H, 2·3; In, 34·7; N, 4·0. $C_8H_8InNO_6$ requires C, 29·2; H, 2·4; In, 35·0; N, 4·2%]. This compound readily loses pyridine at room temperature.

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