Co-ordination Compounds of Indium. Part 35.[1] The Direct Electrochemical Synthesis of Adducts of Indium(III) Halides

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Electrochemical oxidation of anodic indium in non-aqueous media containing halogen may yield either the trihalides (Cl, Br, or I) or the adducts of the trihalides with neutral ligands, depending on the solutes present. Details are given for the preparation of adducts with acetonitrile, pyridine, 2,2′-bipyridine, and triphenylphosphine. The structures of the acetonitrile and pyridine adducts are discussed in the light of new spectroscopic results.

THE addition compounds formed by the interaction of neutral ligands with the indium(III) halides are a well established feature of the co-ordination chemistry of this element, and many such compounds have been reported.[2] The preparation from either anhydrous or hydrated indium trihalide first requires reaction with the ligand in a suitable non-aqueous solvent, and precipitation or other isolation is then followed by recrystallisation to yield the pure product. The halides are obtained from the metal either by high-temperature reaction with halogen, which gives the anhydrous InX_3, or by dissolution in concentrated aqueous hydrohalic acid, which after evaporation yields the hydrated trihalide.

TABLE 1

Experimental conditions for the electrochemical preparation of adducts of indium(III) halides

System [a]	Solution phase composition (volume/cm^3)			Initial voltage (V)	Initial current (mA)	Time of electrolysis (min)	Metal dissolved (g)
	CH_3CN	Other	Ligands				
CH_3CN–Cl_2	50		$Cl_2 + N_2$	2	30	45	2.26
CH_3CN–Br_2	50		4 g Br_2	7	40	60	1.36
CH_3CN–I_2	50		2 g I_2	17	20	85	0.60
bipy–Br_2	15	40 C_6H_6, 30 mg [NEt_4]Br	4 g Br_2, 2 g bipy	30	30	75	0.41
PPh_3–Br_2	15	30 C_6H_6, 30 mg [NEt_4]Br	4 g Br_2, 2 g PPh_3	4	50	105	1.70
py–Br_2 [b]	10	30 mg [NEt_4]Br	15 g Br_2	15	40	180	0.28
dmso–Cl_2 [c]		50 C_6H_6	50 dmso; $Cl_2 + N_2$	15	100	120	0.75
dmso–Br_2 [c]		50 C_6H_6	50 dmso, 2 g Br_2	15	100	120	0.89

[a] bipy = 2,2′-Bipyridine; py = pyridine; dmso = dimethyl sulphoxide. [b] As noted in the text, no adducts were recovered from this experiment. [c] Values from ref. 4.

We have now shown that this simple, but time-consuming series of operations can be circumvented by a direct electrochemical synthesis in which oxidation of an indium anode in a non-aqueous solution cell containing halogen and a neutral ligand yields the appropriate addition compound in good yield and purity. A preliminary report of these and related preparations has already appeared,[3] and details of the electrochemical synthesis of anhydrous indium(III) chloride and bromide have been given elsewhere.[4]

EXPERIMENTAL

General.—Indium [Alfa Inorganics, purity m4N (99.99%)] was hammered into thin sheets, *ca.* 0.5 mm thick; pieces *ca.* 1 × 1 cm were supported on a platinum wire to form the anode of the cell. A stout platinum wire formed the cathode. Other electrochemical techniques were as previously described.[5,6]

Organic solvents were dried over either Linde molecular sieves (acetonitrile, nitromethane, ethyl acetate, and pyridine) or freshly pressed sodium (benzene and diethyl ether). Acetonitrile was redistilled under nitrogen before use. Other materials were used as supplied.

Indium analysis was by atomic absorption spectrophotometry, and halide analysis by Volhard titration. Infrared spectra were recorded over the range 50—4 000 cm^{-1} on either Beckman IR-12 or Perkin-Elmer 180 instruments, using Nujol mulls between potassium bromide or polyethylene plates. Raman spectra were obtained on a Beckman 700 instrument (argon ion excitation, 488.0 nm).

Preparative Work.—The details of solution composition, electrochemical conditions, *etc.* are given in Table 1. The corresponding figures for the electrochemical preparation of dimethyl sulphoxide adducts of the indium trihalides are also quoted in Table 1 for comparison (*cf.* ref. 4 for details). The analytical results for the compounds prepared in the present work are reported in Table 2. Some relevant details of individual preparations are given below. The chemical yields, based on the quantity of indium dissolved, were in the 85—95% range.

It is worth noting that in no case did we observe any attack by halogen on the indium metal before the current was allowed to flow, so that the formation of InX_3 by other than electrochemical oxidation is negligible at room temperature.

Acetonitrile Compounds.—In the case of the *chloride*, it was necessary to cool the cell in an ice-bath to dissipate the appreciable quantities of heat evolved. On completion of the electrolysis, the cell was flushed thoroughly with nitrogen to remove excess of chlorine and excess of solvent was removed *in vacuo* to yield the hygroscopic white solid $InCl_3 \cdot 3CH_3CN$. The preparation of $InBr_3 \cdot 3CH_3CN$ and $InI_3 \cdot 2CH_3CN$ followed similar sequences, except that excess of iodine was not removed before pumping off the solvent. It appeared to be important to stir the solution continuously in the iodide work since the current otherwise dropped to the point at which reaction ceased.

We also noted that when electrolysis was continued in the iodine system beyond the point at which the solution was completely decolorised, deposition of indium(I) iodide occurred at the cathode (Found: In, 47.3; I, 52.3. InI requires In, 47.6; I, 52.4%), clearly indicating reduction of indium(III) species in solution.

2,2′-Bipyridine and Triphenylphosphine Adducts.—In the case of 2,2′-bipyridine, the solid $InBr_3 \cdot 1.5$ bipy (bipy = 2,2′-bipyridine) precipitated during electrolysis and was collected and dried *in vacuo.*

With triphenylphosphine, it was necessary to add ethyl acetate followed by light petroleum to precipitate an oil which subsequently crystallised on trituration. This material was collected, washed with light petroleum, and dried *in vacuo.*

TABLE 2

Analytical results for indium(III) halide adducts prepared electrochemically

Compound *	Found (%)		Calculated (%)	
	Halogen	In	Halogen	In
$InCl_3 \cdot 3CH_3CN$	31.2	33.3	30.6	33.5
$InBr_3 \cdot 3CH_3CN$	49.8	24.5	50.2	24.1
$InI_3 \cdot 2CH_3CN$	65.5	19.7	65.9	19.9
$InBr_3 \cdot 1.5$ bipy	40.5	19.1	40.7	19.5
$InBr_3 \cdot 2PPh_3$	36.0	17.0	36.2	17.3
$InBr_3 \cdot 3$ py	40.2	19.2	40.5	19.4
$InBr_3 \cdot 2$ py	46.3	22.1	46.8	22.4

* The presence of the appropriate neutral ligand was demonstrated in each case by established i.r. spectral criteria.

Pyridine Adducts.—The electrochemical oxidation of indium in the presence of acetonitrile, pyridine, and bromine yielded a dark brown hygroscopic solid (Br, 40.2; In, 9.1%) which we were not able to characterise. It seems probable that species formed by the electrolysis [7] and/or bromination of pyridine play an important part in this system, which was not investigated further.

Two different adducts of pyridine and $InBr_3$ were obtained from the reaction of pyridine with an electrolytically prepared solution of $InBr_3$ in acetonitrile: (a) the addition of pyridine (2 cm^3) to the acetonitrile solution (5 cm^3) gave a yellow oil, which was decanted and treated with benzene; the resultant yellow powder was dried *in vacuo,* and identified as $InBr_3 \cdot 2$py (py = pyridine).

(b) the acetonitrile solution (5 cm^3) was diluted with acetonitrile (15 cm^3), and pyridine (5 cm^3) added, followed by light petroleum (15 cm^3). Stirring produced a white crystalline precipitate of $InBr_3 \cdot 3$py, which was collected and dried *in vacuo.*

RESULTS AND DISCUSSION

Electrochemical Synthesis.—The methods described lead to the synthesis of some typical neutral adducts of the indium trihalides, sufficient in number and variety to leave little doubt that similar techniques could be developed for compounds with other neutral ligands. The yields are good, and gram quantities of product can be synthesised directly from the metal in a few hours with simple apparatus.

In previous papers,[6,8] we have emphasised the importance of the current efficiency (E_F) in identifying the mechanism of an electrochemical oxidation process. For the In–X_2–CH_3CN systems, E_F (defined as mol metal dissolved per Faraday of electricity passed through the cell) was measured at constant current (*ca.* 20 mA) for periods of 1—2 h. The values obtained were 23.4, 7.9, and 4.9 mol F^{-1} for X = Cl, Br, and I respectively. These values are generally higher than those found for transition metals,[6,8] but are in keeping with the mechanism previously suggested, whereby the presumed anode reactions are as in equation (1). Reactions (2) and (3) clearly form a sequence of chain processes, so that

$$X_2^- + M \longrightarrow MX + X^{\cdot} + e^- \qquad (1)$$

$$X^{\cdot} + M \longrightarrow MX \qquad (2)$$

$$MX + X_2 \longrightarrow MX_2 + X^{\cdot} \qquad (3)$$

the high current efficiency is easily understood. The production of indium(I) species by anodic oxidation, of the metal, as required in equations (1) and (2), has been established in earlier work.[3,9] The subsequent formation of the trihalide can be written as (4) and the balance

$$MX + X_2 \longrightarrow MX_3 \qquad (4)$$

between the competing reactions (3) and (4) must depend both on the halogen involved and on the nature of the other stabilising species (ligands) present in the solution phase. The formation of the addition compound requires no special comment.

Structural Considerations.—The structural features of the addition compounds of the indium trihalides has been the substance of a number of studies.[2,10] It is not our purpose to review these earlier studies, but merely to point out some of the important structural points which arise from the present work.

The structure of the *pyridine* compounds $InX_3 \cdot 3$py has been the subject of some debate,[11-14] with a mononuclear six-co-ordinate species generally favoured. The solution properties of such adducts have been discussed earlier,[15] particularly in terms of equilibria such as (5) and (6). The present work confirms that equation (5)

$$InX_3L_3 \rightleftharpoons InX_3L_2 + L \qquad (5)$$

$$InX_3L_3 \rightleftharpoons InX_2L_3^+ + X^- \qquad (6)$$

is valid for X = Br and L = py, since different treatment of the same mother-liquor can yield adducts with either two or three pyridine ligands respectively. A related example with acetonitrile as ligand is discussed below. The main conclusion to be drawn from these, and many similar observations,[2] is that the ease with which equilibria such as (5) are disturbed renders any extrapolation of structural information from solution to solid phases an unreliable procedure.

The *acetonitrile* adducts of the indium(III) halides have not been investigated previously, and indeed the preparation of these compounds has proven surprisingly difficult. It was at one time suggested [12] that $InCl_3$ cannot form a complex with acetonitrile, but a more recent paper reports that $InCl_3 \cdot 2CH_3CN$ was obtained by refluxing indium metal in acetonitrile in the presence of chlorine.[16] In the course of the present work, we obtained this hygroscopic complex by refluxing anhydrous $InCl_3$ (0.5 g) with dry acetonitrile under nitrogen for 5 h; removal of excess of solvent *in vacuo* then yielded the compound in question (Found: Cl, 35.0; In, 37.8. $InCl_3 \cdot 2CH_3CN$ requires Cl, 35.1; In, 37.9%). This compound clearly differs in stoicheiometry from that obtained in the electrochemical work, an observation which again emphasises the importance of equilibria such as equation (5).

Since a complete series is now available, the solid-state structures of the three compounds $InCl_3 \cdot 3CH_3CN$, $InBr_3 \cdot 3CH_3CN$, and $InI_3 \cdot 2CH_3CN$ have been studied spectroscopically. The i.r. spectra of these complexes (Table 3) show that the iodide is both structurally and stoicheiometrically different from its lighter congeners For the chloride and bromide, a six-co-ordinate neutral InX_3L_3 monomer could have either *fac* (C_{2v}) or *mer* (C_{3v}) stereochemistry. The presence of two strong ν(C≡N) vibrations of equal intensity in the i.r. spectrum imply the presence of the *fac* isomer, and in keeping with this there are two readily identifiable ν(In–X) bands in the far i.r. at 328 and 292 (Cl), and 225 and 200 (Br) cm^{-1} {*cf.* the analysis of ν(CO) in $[M(CO)_3L_3]$ complexes}.[17] The ν(In–N) vibrations are then assigned to broad bands at 270 and 235 (Cl), and 274 and 245 (Br) cm^{-1}.

TABLE 3

Infrared spectral data (cm^{-1}) for acetonitrile adducts of indium trihalides

Compound	ν(C≡N)	ν(In–X)	ν(In–N)
$InCl_3 \cdot 3CH_3CN$	2 320vs, 2 291vs	328s, 292 (sh)	270br, 235br
$InBr_3 \cdot 3CH_3CN$	2 295vs, 2 260vs	225s, 200m	274br, 245br
$InI_3 \cdot 2CH_3CN$	2 365m, 2 325s, 2 290s, 2 265m	183vs	240m br, 206s

The iodide compound, in contrast, has a complex set of ν(C≡N) vibrations, which we believe indicates the presence of a *cis*-$[InI_2(NCCH_3)_4]^+$ cation. This species should have four i.r.-active bands in the ν(C≡N) region, and comparison between the observed intensities (Table 3) and those [17] for the analogous ν(CO) modes in *cis*-$[M(CO)_4L_2]$ supports the formulation. Equally there is a strong absorption in the i.r. at 184 cm^{-1}, assigned as ν_3 of InI_4^- (*cf.* ref. 18). We were not able to identify the remaining ν(In–I) modes of the cation but assign a broad band at 240m and a sharper band at 206s cm^{-1} to ν(In–N).

We therefore conclude that the ionic dimer formulation for ' $InI_3 \cdot 2CH_3CN$ ' is correct, and that the structure is very similar to that [19] of $[InI_2(dmso)_4][InI_4]$ (dmso = dimethyl sulphoxide). In this series of acetonitrile adducts then, as in other indium(III) systems,[4] the stability of the InI_4^- anion produces a structure which is different from those of the chloride and bromide analogues.

Solution Properties.—A complete analysis of the vibrational spectra of the acetonitrile adducts was not possible since the Raman spectra of the solid were dominated by extensive random scattering. The Raman spectra of solutions in either acetonitrile (Cl, Br) or methanol (I) are only capable of analysis in the ν(In–X) region, and in each case the main feature was ν_1 of InX_4^- (X = Cl, ν_1 = 328m; Br, ν_1 = 197m; I, ν_1 = 138vs cm^{-1}). Other ν(In–X) bands present were not unambiguously assigned.

The molar conductivities of the three acetonitrile adducts (millimolar concentrations) in nitromethane solution were: $InCl_3 \cdot 3CH_3CN$, 54; $InBr_3 \cdot 3CH_3CN$, 76; $[InI_2(NCCH_3)_4][InI_4]$, 128 cm^2 ohm^{-1} mol^{-1}. As in previous work, these results are best interpreted by hindsight, rather than as giving primary structural information. The value for $[InI_2(NCCH_3)_4][InI_4]$ is close to that normally found for 1 : 1 electrolytes in nitromethane,[20] but the results for the other compounds are most easily understood in terms of equilibria such as equation (6). The Raman spectra imply that the rearrangement reactions in solution may extend further to the formation of InX_4^- species for X = Cl and Br. In the absence of any quantitative information, identification of all the solution species is not presently possible.

This work was supported in part by grants from the National Research Council of Canada, and from the Indium Corporation of America.

[9/1274 *Received, 9th August,* 1979]

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