Preparation of Indium(I) Perchlorate, Tetrafluoroborate, and Hexafluorophosphate

By **Muhammad Ashraf, Abdullah M. Aziz-Alrahman,** and **James B. Headridge,*** Department of Chemistry, The University, Sheffield S3 7HF

Indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate have been prepared by reaction between indium amalgam and sub-stoicheiometric quantities of the appropriate silver(I) salts in acetonitrile, followed by partial evaporation of the solutions. The identities of the salts have been established by quantitative determination of total indium, In^I, and the respective anions.

THE indium(I) ion is thermodynamically unstable to disproportionation in aqueous solution as is evident from the following formal electrode potentials obtained in 3 mol dm^{-3} aqueous perchlorate by Biedermann and Wallin.[1]

$$In^{3+} + 3e^- \longrightarrow In \qquad E_{3/0}' = -0.343 \text{ V} \qquad (1)$$

$$In^{3+} + 2e^- \longrightarrow In^+ \qquad E_{3/1}' = -0.426 \text{ V} \qquad (2)$$

$$In^+ + e^- \longrightarrow In \qquad E_{1/0}' = -0.178 \text{ V} \qquad (3)$$

Indeed Thiel[2] showed that indium(I) chloride and bromide, prepared by solid-state reactions, readily dissolve in water with the formation of indium metal due to the disproportionation of In^I [equation (4)]. Taylor

$$3In^+ \xrightarrow{\text{water}} In^{3+} + 2In \qquad (4)$$

and Sykes[3] prepared aqueous solutions containing *ca.* 3×10^{-4} mol dm^{-3} In^I in 0.01 mol dm^{-3} perchloric acid. In such acid solutions, In^I is unstable being slowly oxidised to In^{III} by hydrogen ion.

For these reasons, simple indium(I) compounds hitherto

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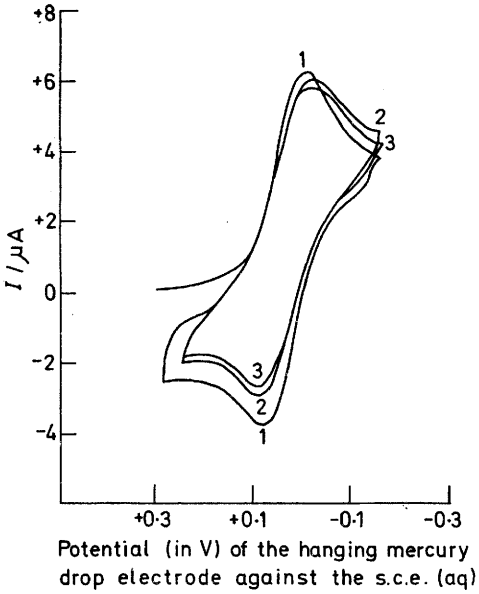
[1] G. Biedermann and T. Wallin, *Acta Chem. Scand.*, 1960, **14**, 594.

[2] A. Thiel, *Z. anorg. Chem.*, 1904, **40**, 280.

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

characterised have been prepared by solid-state reactions. These include the oxide, sulphide, selenide, telluride, fluoride, chloride, bromide, and iodide. It would be difficult to devise a solid-state reaction for the preparation of indium(I) compounds such as the perchlorate. However, such a compound should be readily prepared from a stable solution containing an appreciable concentration of indium(I) cations and low concentrations of indium(III) or other cations.

Headridge and Pletcher[4] predicted and then proved that In^{I} is more stable to disproportionation in acetonitrile than in aqueous solution. They prepared a solution containing 75% In^{I} and 25% In^{III} by reaction of silver(I) perchlorate (1.25 mmol) with indium amalgam (5 mmol of indium). Oxidation of In^{I} to In^{III} by hydrogen ions was not possible, because hydrogen ions were absent from the solution. Indium(I) ions should be even more stable to disproportionation in nitromethane than in acetonitrile because nitromethane has a lower co-ordinating ability for cations than has acetonitrile.[5] Hence it was logical to first attempt the preparation of indium(I) perchlorate from nitromethane solution. It was established that a solution containing In^{I} in nitromethane is readily prepared by shaking a 5×10^{-2} mol dm^{-3} solution of Ag[ClO$_4$] in nitromethane (25 cm^3) with 0.1 mol dm^{-3} indium amalgam (50 cm^3). After the unchanged amalgam and silver had been removed by filtration in a glove-box under dry nitrogen, the presence of In^{I} was verified titrimetrically[4] and by cyclic voltammetry (Figure). Evidence for a reversible one-electron transfer reaction, $\mathrm{In^{I}} \longrightarrow \mathrm{In^{0}} \longrightarrow \mathrm{In^{I}}$, is shown in the Figure. Sweeping the potential of the hanging mercury drop from +0.3 V *versus* the aqueous saturated calomel electrode (s.c.e.) to more positive potentials revealed an irreversible anodic peak for the oxidation of In^{I} to In^{III}. However, the concentration of In^{I} in nitromethane was only *ca.* 20% of the expected concentration and it was concluded that the solubility of indium(I) perchlorate is rather low in nitromethane, and that a better yield of solid compound would be obtained by repeating the preparation in acetonitrile but ensuring that very little In^{III} is produced together with In^{I} by stepping up the concentration of indium in the amalgam to 2 mol dm^{-3}.



Cyclic voltammogram for indium(I) perchlorate in nitromethane. Scan rate, 0.04 V s^{-1}

The preparations of indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate are described in the Experimental section. For the determination of In^{I} in these compounds a slight modification of the titrimetric method used by Headridge and Pletcher[4] was employed. Total indium was determined by atomic-absorption spectrophotometry. All the three anions were determined spectrophotometrically after extraction as ion-association complexes with tris(1,10-phenanthroline)iron(II) into 1,2-dichloroethane. The method was a modification of that used for perchlorate by Fritz *et al.*[6] and for tetrafluoroborate[7] and hexafluorophosphate[8] by Archer *et al.*

RESULTS AND DISCUSSION

Indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate are hygroscopic and soluble in water. Successful preparation of these compounds was only possible when stringent precautions were taken to exclude water from the acetonitrile and from the nitrogen atmosphere of the glove-box where the preparations were made. Duplicate results for the analyses of the compounds are shown in the Table.

These results for the analysis of the three compounds indicate that they are the compounds which we set out to prepare. The presence of silver and mercury in each compound was sought using atomic-absorption and molecular-absorption spectrophotometry based on the mercury(II)–dithizone complex[9] respectively, but in each

Composition of prepared samples of indium(I) perchlorate, tetrafluoroborate, and hexafluorophosphate

	Total indium content (%)		Indium(I) content (%)		Anion content (%)	
Indium(I) compound	found	calc.	found	calc.	found	calc.
Perchlorate	52.9 52.8	53.6	52.6 52.8	53.6	46.2 46.1	46.4
Tetrafluoroborate	56.5 56.3	56.9	56.3 56.1	56.9	42.5 42.8	43.1
Hexafluorophosphate	43.8 43.8	44.2	43.8 43.6	44.2	55.2 55.3	55.8

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[4] J. B. Headridge and D. Pletcher, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 475.

[5] J. B. Headridge, 'Electrochemical Techniques for Inorganic Chemists,' Academic Press, London, 1969, p. 74.

[6] J. S. Fritz, J. E. Abbink, and P. A. Campbell, *Analyt. Chem.*, 1964, **36**, 2123.

[7] V. S. Archer, F. G. Doolittle, and La V. M. Young, *Talanta*, 1968, **15**, 864.

[8] V. S. Archer and F. G. Doolittle, *Analyt. Chem.*, 1967, **39**, 371.

[9] E. B. Sandell, 'Colorimetric Determination of Traces of Metals,' 3rd edn., Interscience, New York, 1959, p. 629.

case these elements were absent. From the Table it can be seen that there was very little if any In^{III} in the three compounds, which are *ca.* 99% pure.

It may be possible to prepare other indium(I) compounds such as the acetate and nitrate using a similar procedure to that employed for the perchlorate, tetrafluoroborate, and hexafluorophosphate. The corresponding silver salts would have to be appreciably soluble in acetonitrile and the indium(I) salts would have to be at least sparingly soluble in acetonitrile. **CAUTION:** Care was always taken in handling the indium(I) perchlorate because it is potentially unstable (detonates, see Experimental section), a good reducing agent being present with an oxidising anion. Similar care would be necessary when working with indium(I) nitrate.

EXPERIMENTAL

Silver(I) perchlorate (B.D.H.) and tetrafluoroborate and hexafluorophosphate (Fluorochem Limited, Glossop) were dried overnight in a vacuum oven at room temperature before use. Acetonitrile was purified and dried using the second method of Walter and Ramaley.[10] All the operations described below in the preparation of the indium(I) solutions were carried out in dry apparatus in a glove-box under an atmosphere of dry nitrogen.

Preparations.—Indium(I) *perchlorate.* Indium amalgam (2 mol dm^{-3}, 50 cm^3) was shaken with a solution (50 cm^3) of 0.1 mol dm^{-3} $Ag[ClO_4]$ in anhydrous acetonitrile for 1 h in a stoppered conical flask. The mixture was transferred to a separating funnel and the indium amalgam removed. The finely divided silver was removed from the solution by triple filtration through dried Whatman No. 1 papers to produce a clear colourless solution. The volume of the solution was reduced to about one fifth by evaporation *in vacuo* and the solution was decanted from the solid which had separated. A pale yellow *product* remained. This was pumped to complete dryness and further dried in a vacuum oven at 90 °C overnight. The yield was *ca.* 200 mg. The preparation was repeated twice with similar yields, and the products were combined and thoroughly mixed to produce *ca.* 0.6 g of salt.

CAUTION: In the initial stages of this work a sample of ' indium(I) perchlorate ' was prepared by complete evaporation of acetonitrile *in vacuo*. The flask containing the product was transferred to a dry glove-box and the crystals of solid material (*ca.* 0.5 g) were removed from the walls of the flask with a glass rod. When an attempt was made to powder the crystals with a glass rod, detonation occurred. It is suggested that no attempt should be made to scale up the described preparative procedure for indium(I) perchlorate.

Indium(I) *tetrafluoroborate and hexafluorophosphate.* The methods were the same as that used for perchlorate except that, after shaking for 1 h, the flask and contents were warmed on a hot plate within the glove-box to *ca.* 60 °C in the preparation of the tetrafluoroborate and to *ca.* 50 °C in the preparation of the hexafluorophosphate. The mixture was maintained at the elevated temperature for 15 min, left to cool to *ca.* 40 °C, and then shaken again for 10 min before transferring to the separating funnel. This modification in the method was required because of the low solubilities of indium(I) tetrafluoroborate and hexafluorophosphate in acetonitrile at room temperature. The total yield of the very pale yellow *tetrafluoroborate* and the white *hexafluorophosphate* was *ca.* 0.4 g in each case.

Analysis of the Products.—Total indium. The total indium contents of the three compounds were determined by atomic-absorption spectrophotometry using a Unicam SP 90 instrument, the indium resonance line at 303.9 nm, and an air–acetylene burner. Two samples of each compound (10—25 mg) were dispensed into a dry weighing bottle inside a dry glove-box and weighed accurately using a five-place semimicrobalance. Each sample was dissolved separately in 1 mol dm^{-3} HCl (10 cm^3) plus a drop of hydrogen peroxide solution (30% w/v) in graduated flasks (100 cm^3) and the solutions were diluted to the marks with 1 mol dm^{-3} HCl. The concentrations of indium in the solutions were determined with reference to a calibration graph for 0—150 $\mu g\ cm^{-3}$ of In^{III} in 1 mol dm^{-3} HCl.

Indium(I). Two samples of each compound (8—20 mg) were dispensed inside the dry glove-box and weighed accurately using a five-place semimicrobalance. Each sample was added separately to conical flasks containing standard potassium dichromate solution (*ca.* 0.017 mol dm^{-3}, 10 cm^3) in excess of that required to oxidise In^I to In^{III}, plus 0.5 mol dm^{-3} H_2SO_4 (2 cm^3), the acid dichromate solution having been previously deoxygenated by passing oxygen-free nitrogen for 10 min. The flask was warmed to *ca.* 40 °C and allowed to cool to near room temperature while maintaining the stream of nitrogen over the surface of the solution. Standardised ammonium iron(II) sulphate solution (*ca.* 0.09 mol dm^{-3} in 0.5 mol dm^{-3} H_2SO_4, 15 cm^3) in excess of that required to reduce unchanged dichromate, was added together with distilled water (30 cm^3), 5 mol dm^{-3} orthophosphoric acid (6 cm^3), and three drops of barium *N*-phenylanaline-2-sulphonate indicator (0.2% w/v). The unchanged Fe^{II} was titrated with the standard solution of potassium dichromate.

Anions. The following method was used for the determination of tetrafluoroborate. Standard solutions of 10, 20, 30, 40, 50, and 60 $\mu g\ cm^{-3}$ of tetrafluoroborate anion in 0.2 mol dm^{-3} potassium fluoride–0.2 mol dm^{-3} hydrofluoric acid (fluoride buffer solution) were prepared from sodium tetrafluoroborate dried in a vacuum oven at 60 °C overnight. To each solution (10 cm^3) in Polythene bottles were added freshly prepared 0.01 mol dm^{-3} tris(1,10-phenanthroline)-iron(II) sulphate solution (5 cm^3) and 1,2-dichloroethane (20 cm^3), and the solutions were shaken in the bottles for 5 min. They were then transferred to Polythene separating funnels, where the organic layers were separated. These organic solutions were transferred to centrifuge tubes, and centrifuged for 2 min to remove any of the aqueous phase still present. A suitable volume was taken from each organic solution for measuring the absorbances in 1-cm glass cells at 520 nm. From these results the calibration graph was drawn. Two samples of indium(I) tetrafluoroborate (*ca.* 20 mg) were dispensed inside the glove-box and weighed accurately using a five-place semimicrobalance. The samples were separately dissolved in volumes (250 cm^3) of fluoride buffer solution and the resulting solutions (10 cm^3) were treated in the same way as the standard solutions. The concentrations of these solutions were determined from the calibration graph.

The hexafluorophosphate content of the sample of indium(I) hexafluorophosphate was determined in duplicate using the same method and *ca.* 10 mg of salt. The standard

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[10] M. Walter and L. Ramaley, *Analyt. Chem.*, 1973, **45**, 165.

solutions were prepared from sodium hexafluorophosphate which had been dried overnight in a vacuum oven at 60 °C. The perchlorate content of the sample of indium(I) perchlorate was determined in duplicate in a similar way using *ca.* 25 mg of salt in water (500 cm^3). It was not necessary to work in fluoride buffer solution because perchlorate is stable to hydrolysis. The standard solutions were prepared from AnalaR sodium perchlorate which had been dried overnight in a vacuum oven at 60 °C.

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