Direct Electrochemical Synthesis of Indium Compounds

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Summary Cationic, neutral, and anionic complexes of indium can be prepared by the direct oxidation of the highly charged metal by the appropriate solute in an organic solvent.

WE have recently reviewed the synthesis of co-ordination complexes of indium in its different oxidation states.[1] In many cases, indium metal was dissolved in the appropriate aqueous acid to yield the hydrated trihalide, or oxidized with a halogen to the anhydrous InX_3.[2] The reaction of these halides in aqueous or nonaqueous solution leads to the formation of anionic and neutral In^{III} complexes. Similarly, cationic complexes can be prepared *via* hydrated In^{III} salts, which are themselves obtained by dissolving the metal in aqueous nitric[3] or perchloric[4] acid. A normal cycle of reactions would be oxidation of the metal, evaporation to dryness, dissolution in an organic solvent, addition of a suitable reagent, precipitation, and recrystallization.

We now report that this cycle of operations can be circumvented by a direct electrochemical process, in which the indium acts as the anode in an unusual cell. The cathode is normally a platinum wire or sheet, but the novelty of this system lies in the solution phase, which is an aromatic solvent (normally benzene) containing 10—20% alcohol (100 ml total). For anionic complexes, the solutes are normally the appropriate halogen and the tetra-alkylammonium halide, but for neutral complexes, a small quantity of Et_4NClO_4 is added to increase the current flow. The applied voltage is 50—100 V, significantly higher than in most electrochemical reactions; the current under these conditions is 20—100 mA. Electrolysis over a period of 1—3 h is sufficient to produce gram quantities of the compounds. All the experiments involve substances which are insoluble in the solvent, and the products are obtained as crystalline material at the bottom of the reaction vessel. Reactions were carried out both under nitrogen and in air, with temperature maintained at or below 25 °C.

The following compounds are representative of those prepared by this technique: (1) Crystalline trihalides, InX_3 (X = Cl, Br, or I) were obtained with halogen as the solute reagent. The reaction was smooth, except that, in the case of $InCl_3$, it was necessary to keep the chlorine concentration low by dilution with nitrogen in order to minimise attack on the solvent. In the presence of water, $InCl_3.3H_2O$ was obtained. When ethanol was replaced by Me_2SO the adduct $InX_3.3Me_2SO$ (X = Cl or Br) was the only product.[2] Presumably one could prepare other InX_3 adducts by suitable choice of solutes. (2) The compound $In(acac)_3$ was obtained by electrochemical oxidation of the metal in the presence of a benzene–ethanol solution of acetylacetone.[5] (3) For $[In(Me_2SO)_6](ClO_4)_3$ the liquid phase was a mixture of $HClO_4$ (60%, 25 ml), MeOH (25 ml), and Me_2SO (50 ml). Nitrogen was bubbled through the solution, and the temperature of the cell was maintained at 0 °C for 3 h. (4) Anionic halide complexes, $(Et_4N)_2InCl_5$[6] and $(Et_3PhN)_2InCl_5$ were obtained from a benzene–methanol solution of R_4NX ($R_4 = Et_4$ or Et_3Ph) and Cl_2 in 2—3 h. In the presence of Et_4NI and I_2, the oxidation of indium proceeds only to the +1 state, and the products are, *e.g.*, $Et_4N[InI_2]$, similar to those discussed elsewhere.[7]

All these syntheses are rapid and simple and have advantages over those described earlier. The mechanism of the reactions is not clear yet, but it seems that the analogy of aqueous phase anodic electrochemical oxidation of the metal may be inappropriate. The method is not restricted to the element indium, since we have prepared a series of anionic complexes of a number of transition and main group metals, using Et_4NBr and Br_2 in benzene–methanol as the solution phase. Extension of the method to neutral or cationic complexes of these elements should be possible by adjusting the solution conditions, thereby opening up a direct electrochemical route to a wide variety of inorganic molecules.

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