New Synthetic Routes to Anionic Indium(I) Halide Complexes

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Summary Stable compounds of both $[\text{InX}_3]^{2-}$ and $[\text{InX}_2]^-$ can be obtained either from cyclopentadienylindium(I), or by the electrolytic oxidation of indium metal in organic media.

PREVIOUS publications[1,2] have described the simple preparation of salts of the anionic indium(I) complexes $\text{InX}_3{}^{2-}$ (X = Cl, Br, I) by refluxing a methanolic solution of $\text{Me}_2\text{bipy.X}_2$ ($\text{Me}_2\text{bipy}^{2+}$ = *NN'*-dimethyl-4,4'-bipyridinium cation) with a suspension of InX. Later studies have shown that this method is not in fact a general one, in that other organic cations do not react as readily as does $\text{Me}_2\text{bipy}_2{}^+$. We now report two new synthetic routes to these and other indium(I) complexes.

In the first study, the soluble organoindium(I) compound cyclopentadienylindium(I)[3] [In(cp)] in benzene containing a small amount of ethanol was treated with $[\text{R}_4\text{N}]\text{X}$ and HX in quantities calculated according to equation (1), where

$$[\text{In(cp)}] + n\text{Cat.X} + \text{HX} \rightarrow \text{cpH} + (\text{Cat})_n\,[\text{InX}_{n+1}] \qquad (1)$$

Cat is an organic cation. The solutions were generally mixed at room temperature; finely divided crystals formed when the mixture was cooled to 0 °C for about 30 min. For X = I and Cat = 1,2-bis(methyldiphenylphosphonio)ethane, the product from reaction (1) is $[\text{MePh}_2\text{PC}_2\text{H}_4\text{PPh}_2\text{Me}][\text{InI}_3]$, analogous to the compounds reported previously. When the cation is Et_4N^+, however, the products for X = Cl, Br, or I are the salts $[\text{Et}_4\text{N}][\text{InX}_2]$ which contain previously unknown anionic indium(I) complexes. Vibrational spectroscopy demonstrates that the $\text{InX}_2{}^-$ anions are isostructural with the tin(II) halides.

We have noted elsewhere that a characteristic property of indium(III) is that the stoicheiometry of the anionic halide complexes is dependent upon the nature of the cation.[2,4,5] The preparation of both $\text{InX}_2{}^-$ and $\text{InX}_3{}^{2-}$ species shows that this variation in stoicheiometry also extends to the analogous indium(I) species.

An alternative preparative route to the iodoindium(I) species $[Et_4N][InI_2]$ involves the electrolytic oxidation of indium metal. Electrolysis between an indium anode and a platinum cathode, with a solution of $Et_4NI + I_2$ in benzene–methanol, resulted in the formation of a purple layer of InI on the anode surface. Further electrolysis brought about the complete discharge of the iodine colour and the disappearance of InI, and subsequent precipitation of crystals of $[Et_4N][InI_2]$. The salt $[MePh_2PC_2H_4PPh_2Me][InI_3]$ (see above) has also been obtained by this electrolytic technique. The method cannot apparently be used to produce indium(I) complexes with bromide or chloride, since experiments analogous to those just described gave rise to indium(III) species, which may be either neutral or anionic depending upon the solution conditions. In addition, the products from these latter experiments depend on current density and temperature.

Both synthetic routes should be of general application in co-ordination chemistry. In addition, we find that the InX_3^{2-} and InX_2^{-} anions are useful starting materials for the synthesis of both indium(I) and indium(III) compound with other ligands, either by substitution or oxidation.[6]

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