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STUDIES IN THE COORDINATION CHEMISTRY OF INDIUM(III)

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The general chemical behaviour of the elements of group IIIB (B, Al, Ga, In, Tl) has long been established, but although there has been a considerable amount of work on the acceptor properties of the neutral compounds, especially for boron, aluminium and gallium[1,2], much less attention has been paid to those complexes which can be regarded as being formed from a tripositive metal ion and donor ligands. Furthermore, in terms of the adducts of MX_3 compounds, indium has been less studied than its lighter homologues, possibly because the addition compounds with neutral ligands rarely have the 1:1 stoichiometry which renders the thermodynamic treatment of such compounds so attractive. Because of this general lack of information on the coordination chemistry of indium(III), an investigation into the formation of coordination compounds has been undertaken, and some of the results obtained so far are reported in this paper. In particular, we are interested in the possible coordination numbers of indium(III), generally believed to be four or six[3].

1. CATIONIC COMPLEXES[4]

During studies of the indium(III) species present in various aqueous solutions, it was found[5] that in dilute perchloric acid one has the aquo-cation $[In(H_2O)_6]^{3+}$. The crystalline solid obtained from more concentrated solutions is $In(ClO_4)_3 \cdot \sim 8H_2O$, which has been used as the starting material for the preparation of a series of compounds containing In^{III} cationic complexes. In each case, perchlorate was the only anion present, and was shown from the infrared spectrum to be present entirely as ClO_4^-, so that the stoichiometry of the cation leads to the coordination number of In^{III}.

The preparative method generally involved mixing hydrated indium(III) perchlorate in some suitable organic solvent (ethanol, ether, ethyl acetate) with a similar solution of the ligand; crystals were precipitated immediately or after refluxing. The following tripositive complex cations were obtained:

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$[In(dipy)_3]$, $[In(phen)_3]$, $[In(en)_3]$, $[In(trip)_2]$
$[In(urea)_6]$, $[In(dmso)_6]$, $[In(dimac)_6]$
$[In(thiourea)_6]$
$[In(Ph_3P)_4]$, $[In(Ph_3PO)_4]$, $[In(Ph_3As)_4]$, $[In(diphos)_2]$

Ligands: dipy = 2,2′-dipyridyl; phen = 1,10-phenanthroline;
trip = 2,2′,2″-tripyridyl;
en = ethylenediamine; dmso = dimethylsulphoxide;
dimac = N,N-dimethylacetamide;
diphos = bis(diphenylphosphino)ethane.

In general, the In^{III} cation is apparently six-coordinate with ligands whose interaction is predominantly by σ-donation; when π-bonding is likely, four-coordinate species are obtained. (See below).

In a number of cases it was not possible to obtain products by the above methods, or variants of them. Ligands which came into this category included ammonia, pyridine, dimethyl sulphide and diphenyl sulphide; with tributyl phosphine, a waxy product was obtained which could not be purified by recrystallisation.

2. ANIONIC HALIDE COMPLEXES

The extraction of indium(III) from aqueous solutions of hydrofluoric, hydrochloric, hydrobromic, hydriodic and hydrocyanic acids into chloroform solutions of methyldioctylamine has been studied by radioactive tracer methods[6]. No extraction was observed in the fluoride system, but so far it has not been possible to establish the reasons for this.

With the remaining acids, the distribution coefficient (D_{In}) increases in the order HCl < HBr < HI ≈ HCN. By studying the dependence of D_{In} on the concentration of amine, it is possible to obtain the charge on the extracted anion. With all three halo-acids, singly and triply charged anions are identified; doubly charged species may also be present, although of course values of $n = 2$ in this type of experiment may simply arise by the appropriate mixing of $n = 1$ and $n = 3$. A detailed consideration of the extraction data in these and earlier experiments leads to the conclusion that the triply charged species is InX_6^{3-}. Similarly, the singly charged anion in the organic phase is thought to be InX_4^-, but in aqueous solution the corresponding species is $[InX_4(H_2O)_2]^-$. This latter is a member of a series of $InX_4L_2^-$ anions, isoelectronic with the known neutral adducts of tin(IV) with donor ligands[7]; we have prepared $Et_4N[InCl_4L_2]$ where L is urea or thiourea[8]. As noted above, the existence of a doubly charged anion is not firmly established, although it is worth noting that $[InCl_5 \cdot H_2O]^{2-}$ is known to be isostructural with the corresponding six-coordinate iron(III) anion[9]. The existence of such an anion in aqueous solution would imply equilibria between three six-coordinate anions, $[InX_4(H_2O)_2]^-$, $[InX_5 \cdot H_2O]^{2-}$, and $[InX_6]^{3-}$.

In addition to the known crystalline salts which presumably contain indium(III)–halogen complex anions, there is a series of double salts, reported by Ekeley and Potratz[10], which can be formulated as complexes of InX_4^-, InX_5^{2-}, InX_6^{3-} and InX_7^{4-}. We are attempting to establish the structure of these anions by various methods, and to investigate the influence of factors such as ligand and cation size, etc., on the stoichiometry and stability of the anion.

Although indium(III) extracts well from aqueous hydrocyanic acid solution, it was not possible to identify the extracted anionic complex because of the complexity of the amine—cyanide species in the organic phase.

3. INDIUM(III) NITRATE STUDIES[11]

Indium(III) nitrate[11] is known as both the anhydrous compound[12] and as the product obtained by crystallising a nitric acid solution; this latter compound we find to be $In(NO_3)_3 \cdot 3H_2O$.

Indium(III) in aqueous nitric acid could not be extracted into either tri-*n*-butyl phosphate or methyldioctylamine in chloroform; transference experiments showed that no anionic indium species are present in these aqueous solutions. A double salt, $NH_4NO_3 \cdot In(NO_3)_3$ has been reported[13], but it was not found possible to repeat this work. Partial crystallisation of aqueous solutions of a series of tetra-alkylammonium nitrates and indium nitrate in nitric acid gave a product containing an anionic indium nitrate species only with $Et_4N \cdot NO_3$; this product was $Et_4N[In(NO_3)_4]$, which is stable up to 270°, at which temperature it explodes violently.

Reaction of indium(III) nitrate hydrate in ethanol with a number of donor ligands in the same solvent gave the following products, which precipitated immediately on mixing the solutions:

$[In(dmso)_6](NO_3)_3$ $[In(urea)_6](NO_3)_3$
$[In(en)_3](NO_3)_3$
$[In(dipy)_2(NO_3)_2]NO_3$
$[In(phen)_2(NO_3)_2]NO_3$

The complexes with dimethylsulphoxide, urea and ethylenediamine are clearly the nitrate analogues of the perchlorate species, discussed earlier[4]. The formulation given for the 2,2′-dipyridyl and 1,10-phenanthroline complexes is based on analysis, infra-red spectrum and the typical 1:1 electrolyte conductivity in nitromethane. Further work on these systems, and on the complexes obtained via aqueous solution, is continuing.

4. ADDUCTS OF INDIUM(III) HALIDES[14]

Previous workers have reported a number of adducts formed by indium(III) chloride, bromide and iodide and a series of variously assorted ligands*. The majority of these are of the type $InX_3 \cdot L_3$, where L is a monodentate ligand, but Fairbrother and his co-workers[16] have reported $InX_3 \cdot L_2$ for a number of ethers and thioethers. Using conventional preparative methods, we have now obtained the following compounds.

TABLE I

STOICHIOMETRY OF ADDUCTS OF NEUTRAL LIGANDS WITH INDIUM(III) CHLORIDE, BROMIDE AND IODIDE[14]

Ligand	$InCl_3 \cdot L_x$	$InBr_3 \cdot L_x$	$InI_3 \cdot L_x$
Urea	1 : 3	1 : 3	(a)
Dimethylsulphoxide	1 : 3	1 : 3	1 : 2
Pyridine-N-oxide	1 : 3	(b)	(b)
N,N-Dimethylacetamide	1 : 2.5	1 : 1.5	1 : 1.5
Thiourea	1 : 3	1 : 3	(a)
Triphenylphosphine	1 : 2	1 : 2	1 : 2
Triphenylphosphine oxide	1 : 2	1 : 2	1 : 2
1,2-Bis(diphenylphosphino)ethane	(a)	1 : 1	1 : 1
2,2'-Dipyridyl	1 : 1.5	1 : 1.5	1 : 1.5

(a) preparation attempted, but no satisfactory product obtained.
(b) preparation not attempted.

Although structural studies on these compounds are as yet incomplete, some comments can be made on these stoichiometries. Firstly, with the exception of $InI_3 \cdot (dmso)_2$, apparently six-coordinate species are obtained with those ligands (dimethylsulphoxide, urea, thiourea) which form cations InL_6^{3+} in which indium(III) is also six-coordinate. However, in solution in solvents such as nitromethane, these compounds show conductivities somewhat lower than 1:1 electrolytes, so that some dissociation is clearly occurring. The *N,N*-dimethylacetamide adducts are of unusual stoichiometry, which at present we believe to indicate the formation of dimeric species involving bridging by halide and/or *N,N*-dimethylacetamide.

Complexes of the type InX_3L_2 are obtained with ligands which as noted above, give four-coordinate indium(III) cations. Our results with 2,2'-dipyridyl are not in agreement with those reported by Sutton[17], who found $In(dipy)_3X_3$ by a rather different preparative method. It is worth noting that $TlCl_3 \cdot 1.5$ dipy has recently been prepared[18], and that indium(III) thiocyanate also gives $InX_3 \cdot 1.5$ dipy (see below). The structure of this group of compounds is clearly a most important and as yet unresolved problem.

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* For example see ref. 15.

5. INDIUM(III) THIOCYANATE STUDIES[19]

Thiocyanates of group IIIB elements have been prepared by non-aqueous reactions[20], but we were not able to obtain $In(CNS)_3$ by such a route; in fact, addition of barium thiocyanate to indium sulphate in aqueous solution followed by evaporation yielded the desired product, which is insoluble in dry acetone, alcohol and other organic solvents. By a series of suitable reactions, however, adducts of the type $In(CNS)_3 \cdot L_3$ have been obtained with urea, dimethylsulphoxide, *N,N*-dimethylacetamide, triphenylphosphine oxide, pyridine, 4-methyl-pyridine and thiourea. With ethylenediamine, the product $[In\,en_3](CNS)_3$ is again analogous to the cationic species obtained with nitrate and perchlorate. As in the indium trihalide systems, 2,2′-dipyridyl and, in this case, 1,10-phenanthroline, yielded $In(CNS)_3 \cdot 1.5$ dipy and $In(CNS)_3 \cdot 1.5$ phen.

Complexing between indium(III) and thiocyanate ion in aqueous solution is well established[21]. As part of a study of the effect of cation size on the crystalline salts, we have obtained $(Me_3NH)_3[In(CNS)_6]$, and are attempting analogous preparations with other organic cations

6. BONDING IN INDIUM(III) COMPLEXES

Since the complexes obtained are colourless, and diamagnetic, a simple experimental investigation of the electron distribution around the metal is not possible. In fact, with indium as with other post-transition group metals, a detailed understanding of the bonding in its complexes is lacking. In particular, in situations where a distinction between σ-bonding and possible π-bonding is required, the lack of a diagnostic test of this latter phenomenon is especially acute. In the case of tris-acetylacetonate indium(III), it has recently been shown[22] that earlier conclusions about π-bonding in this, and similar compounds, based on nuclear magnetic resonance studies, are not firmly founded. Our present conclusion is that the presence of π-bonding in some indium(III) complexes is in keeping with the known facts, but that definite proof has not yet been obtained.

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