# Co-ordination Compounds of Indium. Part XXII.[1] Anionic Complexes derived from the Lower Halides of Indium

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The halide salts of the dispositive *NN'*-dimethyl-4,4'-bipyridinium cation ($Me_2bipy,X_2$; X = Cl, Br, or I) react with indium monohalides to give salts of the trihalogenoindate(I) anions $Me_2bipy,InX_3$, in which the anion is isoelectronic with $SnX_3^-$ and $SbX_3$. With indium trihalides the products are either $Me_2bipy,[InCl_5]$ or $Me_2bipy^{2+} + InX_4^- + X^-$ (X = Br or I); the $InCl_5^{2-}$ anion has $C_{4v}$ symmetry in the salt prepared, and this result is discussed in terms of earlier studies of this anion. The indium dihalides yield a mixture of $In^I$ and $In^{III}$ anions. The Raman spectra are reported for the anionic complexes prepared, for the indium monohalides, and for indium dibromide and di-iodide.

One of the features of the chemistry of indium is the dearth of preparative and structural studies of complexes of the element in its lower oxidation states. In the +I state, simple binary compounds (halides, oxide, sulphide) are known,[2] but the only complexes reported in the literature are the adducts of the monohalides with ammonia,[3] aniline,[4] and morpholine,[4] of the type InX,2L (L = $NH_3$ or morpholine) or InX,4L (L = aniline). The redox reactions of indium(I) species in electrolytically prepared aqueous solutions have recently been described in detail.[5] Some insertion reactions of the indium monohalides into S–S [6] and C–X (X = Br [7] or I [8]) bonds have also been investigated. Indium(II) compounds have been the subject of curiosity for some time, but only recently has any structural information been available.

This paper reports the preparation of anionic halide complexes by the reaction of the neutral indium mono-, di-, and tri-halides with the corresponding *NN'*-dimethyl-4,4'-bipyridinium halide ($Me_2bipy^{2+}X_2^-$). With indium(I) halides, the products are salts of the trihalogenoindate(I) anions, whose preparation has been reported briefly elsewhere.[9] Indium(III) halides give rise to species which can be compared directly with the anionic indium(III) halide complexes discussed earlier;[10] some interesting changes result from the use of a dipositive, rather than a monopositive, organic cation The reaction of indium(II) halides with $Me_2bipy,X_2$ yields mixtures of indium(I) and indium(III) complexes, in keeping with the formulation of these dihalide compounds as mixed oxidation state species.

The cation used in this work, *NN'*-dimethyl-4,4'-bipyridinium, is one of the few readily available dipositive organic cations. The preparation of its salt was first described by Michaelis and Hill,[11] who studied these species in terms of the use of the cation as a redox indicator. The colour changes observed in the preparation of indium(I) complexes (see below) are clearly associated with these indicator properties.

*Trihalogenoindate*(I) *Anions*.—Anionic complexes of tin(II) of the type $SnX_3^-$ (X = Cl, Br, or I) have been reported,[12] and it seemed likely that the isoelectronic indium(I) species might also be stabilised in some suitable solid lattice. The obvious starting materials, the indium(I) halides, are apparently insoluble in most solvents which provide a useful test of complex formation; for example, indium monochloride does not dissolve in molten tetraethylammonium chloride, so that this route to $[In^ICl_n]^{(n-1)-}$ anions is not available. Each of the monohalides however reacted smoothly when a suspension in methanol was stirred under nitrogen with a solution of $Me_2bipy,X_2$. After a few minutes the suspension became blue, and after 2—3 h a clear (blue) solution was obtained; this colour could be removed by adding a trace of (say) iodine to the solution. It seems probable that a small amount of disproportionation of $In^I$ to $In^0 + In^{III}$ occurs, and that the cation indicator responds to the presence of $In^0$; a trace of oxidising agent restores the cation to its colourless form. In each case, evaporation of the solution gave the $(Me_2bipy)$ $[InX_3]$ salt. (See Table 1 for analytical results.)

Following the work of Benoit *et al.*[13] on germanium(II), we also investigated the electrolytic reduction of indium(III) in conc. hydrochloric acid, both preparatively and polarographically, but found no evidence to suggest that indium(I) species could be obtained in this way.

The molar conductivities of all three $InX_3^{2-}$ compounds were measured in either acetonitrile or nitrobenzene solution, as dictated by the solubilities. For X = Cl and Br, the molar conductivities in acetonitrile at *ca.* mM concentration were 97 and 85 $\Omega^{-1}$ $cm^2$ respectively; other 1 : 1 electrolyte indium complexes [14]

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gave values in this solvent in the range 90—140 $\Omega^{-1}$ cm$^2$. For (Me$_2$bipy)[InI$_3$], the molar conductivity in nitrobenzene was 25 $\Omega^{-1}$ cm$^2$, to be compared with a reported range[15] of 20—40 $\Omega^{-1}$ cm$^2$ for 1 : 1 electrolytes. The formulation of these salts as 1 : 1 electrolytes is therefore confirmed by these results. The molar magnetic susceptibilities of the three salts were $-246$, $-287$, and $-132 \times 10^{-6}$ (c.g.s.u.) for the chloride, bromide, and iodide respectively, values which confirm the expected diamagnetism of the compounds prepared.

TABLE 1

Analytical results for anionic indium complexes

| | Found (%) | | | | | Required (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Salt[a] | C | H | N | Halogen | In | C | H | N | Halogen | In |
| C[InCl$_3$] | 36·7 | 3·7 | 7·0 | 26·4 | 28·4 | 35·4 | 3·4 | 6·9 | 26·2 | 28·2 |
| C[InBr$_3$] | 26·8 | 2·7 | 5·1 | 44·3 | 21·3 | 26·6 | 2·6 | 5·2 | 44·4 | 21·2 |
| C[InI$_3$] | 21·3 | 2·2 | 3·9 | 55·2 | 16·2 | 21·1 | 2·1 | 4·1 | 55·9 | 16·8 |
| C,InCl$_4$ | 32·8 | 3·2 | 5·6 | 32·1 | 25·8 | 32·5 | 3·2 | 6·3 | 32·1 | 25·9 |
| C,InBr$_4$ | 23·0 | 2·4 | 4·4 | 51·5 | 18·5 | 23·2 | 2·3 | 4·5 | 51·5 | 18·5 |
| C,InI$_4$ | 17·7 | 1·7 | 3·2 | 62·6 | 14·7 | 17·8 | 1·7 | 3·5 | 62·8 | 14·2 |
| C[InCl$_5$] | 30·5 | 2·9 | 5·5 | 37·4 | 24·2 | 30·1 | 2·9 | 5·9 | 37·1 | 24·0 |
| C,InBr$_5$ | 20·6 | 2·0 | 3·7 | 56·7 | 16·7 | 20·6 | 2·0 | 4·0 | 57·1 | 16·4 |
| C,InI$_5$ | 15·4 | 1·5 | 3·1 | 67·5 | 12·3 | 15·4 | 1·5 | 3·0 | 67·9 | 12·3 |

[a] C = *NN'*-Dimethyl-4,4'-bipyridinium cation.

*Vibrational Spectra of Indium Monohalides and Trihalogenoindate*(I) *Anions*.—The Raman spectra of the solid indium monohalides showed the following bands:

| | |
|---|---|
| InCl | 86sh, 102w, 234m |
| InBr | 38w, 47s, 68ms, 86ms |
| InI | 39mw, 78vs, 105mw, 135w, 211s cm$^{-1}$ |

Two of these solids (bromide[16] and iodide[17]) have been shown to have thallium(I) iodide layer structures.[18] No attempt was made at assigning the bands observed; the more important point is that the InX$_3^{2-}$ complexes have very different spectra in this region.

Table 2 gives the Raman spectra of the three InX$_3^{2-}$ anions, together with the appropriate results[19-21] for the isoelectronic SnX$_3^-$ and SbX$_3$ species. The assignments are based on an assumed $C_{3v}$ symmetry, although Wharf and Shriver[21] have questioned this assumption for the SnBr$_3^-$ and SnI$_3^-$ anions, for which they suggest $C_s$ symmetry. The similarities in the spectra within a given group of MX$_3$ species supports the suggestion that the InX$_3^{2-}$ anions are isostructural with the analogous tin(II) and antimony(III) compounds. These assignments for InX$_3^{2-}$ species are supported by force constant calculations.[22]

*Reactions Involving Indium Trihalides*.—In order to elucidate the nature of the products of the reaction of Me$_2$bipy,X$_2$ with the corresponding indium dihalides (see below), it was first necessary to investigate the reaction of these salts with the neutral indium(III) halides. The results are interesting in terms of the comparisons with earlier studies of anionic indium(III) halide complexes.[10] With each trihalide, the reaction product has the stoicheiometry Me$_2$bipy,InX$_5$, but spectroscopic investigations show that only in the case of the chloride is an InX$_5^{2-}$ anion actually present.

The Raman spectra of the bromide and iodide compounds have bands at 196s, 232w, 74w, and 84w (bromide), and 137vs, 197m, 181m, and 56w cm$^{-1}$ (iodide), in addition to the many emissions associated with the cation. Salts of the InBr$_4^-$ ion have Raman bands[10] at 200s ($\nu_1$, $a_1$), 237wm ($\nu_3$, $f_2$), and 79 ($\nu_4$, $f_2$), while for InI$_4^-$, the analogous modes are at 139s, 186w, and 58 cm$^{-1}$. We therefore conclude that the solid state lattices of the compounds Me$_2$bipy,InX$_5$ (X = Br or I) are in fact Me$_2$bipy$^{2+}$ + InX$_4^-$ + X$^-$, with the InX$_4^-$ anion in some site symmetry lower than tetrahedral, so that some splitting of $\nu_3$ occurs. This conclusion is in keeping with earlier work,[10] in which the compound (Me$_4$N)$_2$InBr$_5$ was shown to consist of 2Me$_4$N$^+$ + InBr$_4^-$ + Br$^-$ by similar arguments. Since no crystalline anionic iodo-complexes of indium(III) with a co-ordination number greater than four have been reported, the failure to obtain InI$_5^{2-}$ is not surprising.

TABLE 2

Raman spectra of InX$_3^{2-}$ anions, and vibrational spectra of SnX$_3^-$ and SbX$_3$ analogues (in cm$^{-1}$)

| | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | Ref. |
|---|---|---|---|---|---|
| X = Cl | | | | | |
| In$^{\text{I}}$ | 252 | 102 | 185 | 97 | |
| Sn$^{\text{II}}$ | 297 | 128 | 256 | 103 | 19 |
| Sb$^{\text{III}}$ | 345 | 176 | 322 + 316 | 154 + 145 + 141 | 20 |
| X = Br | | | | | |
| In$^{\text{I}}$ | 177 | 74 | 149 | 46 | |
| Sn$^{\text{II}}$ | 211 | 83 | 181 | 65 | 19 |
| Sb$^{\text{III}}$ | 246 | 113 | 229 | 92 | 20 |
| X = I | | | | | |
| In$^{\text{I}}$ | 136 | 78 | 110 | 40 | |
| Sn$^{\text{II}}$ [a] | 152 | 60 | 128 | 50 | 21 |
| Sb$^{\text{III}}$ | 160 | 67 | 138 | 43 | 20 |

[a] Bands at 137 and 50 (?) cm$^{-1}$ are assigned to $\nu_5$ and $\nu_6$ in $C_s$ symmetry by these authors.

In contrast, the relevant part of the Raman spectrum of Me$_2$bipy[InCl$_5$] is very similar to that reported for the

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salt $(Et_4N)_2[InCl_5]$ by a number of authors. Adams and Smardzewski [23] have carried out a thorough analysis of the vibrational spectrum of this compound, and made assignments in terms of the $C_{4v}$ symmetry of the anion, established by $X$-ray crystallography.[24] Adams and Smardzewski report nine Raman active lines between 300 and 100 $cm^{-1}$, at 294, 287, 273, 193, 165, 145, 141, 123, and 107 $cm^{-1}$. For $Me_2bipy[InCl_5]$, we find Raman modes at 294m, 281m, 275m, 194w, 142w, 124m, and 105w $cm^{-1}$, and we therefore conclude that the latter solid contains the $C_{4v}$ $[InCl_5]^{2-}$ anion.

This conclusion is of some importance in terms of the earlier discussion [24] of this anion, whose structure differs from the isoelectronic species $SnCl_5^{2-}$ and $SbCl_5$, which have $D_{3h}$ symmetry.[25,26] More recently, the $CdCl_5^{2-}$ anion has also been found to have a trigonal bipyramid structure,[27] emphasising once again the anomalous structure of $InCl_5^{2-}$. The suggestion [24] was made earlier that the $C_{4v}$ symmetry might have been the result of lattice effects associated with the $Et_4N^+$ cation, although this proposal was not supported by some incomplete spectral results [10] on salts with the cations $Me_4N^+$, $MePh_3N^+$, and $BzPh_3P^+$, for which $C_{4v}$ symmetry also appeared probable. The present data show clearly that a severe change of cation from $2Et_4N^+$ to the large dipositive $Me_2bipy^{2+}$ does not alter the $C_{4v}$ symmetry of $InCl_5^{2-}$, and lattice effects can seemingly therefore be rejected in any discussion of this problem; the explanation for the fact that $InCl_5^{2-}$ is not isostructural with its isoelectronic $d^{10}$ congeners is not apparent at the present time.

*Reactions Involving Indium Dihalides.*—The structure of the indium dihalides has been the subject of considerable discussion. The compounds are not simple $M^{2+}$ salts, since they are diamagnetic, and the two formulae most strongly urged have involved either a metal–metal bonded dimer $X_2M{-}MX_2$, or an ionic dimer of mixed oxidation state $M^I[M^{III}X_4]$. Both spectroscopic and chemical evidence have been advanced in support of each of these formulations.

Unlike the gallium dihalides, for which magnetic, $X$-ray structural and vibrational spectral [28-31] evidence has now established that $Ga[GaX_4]$ (X = Cl, Br, or I) is indeed the structure in the solid state, in solution, and in melts, the literature on the indium–chloride system is extensive and confusing. There are disagreements as to the details of the indium–chloride phase diagram, and as to the stable solid state species; $InCl_2$, $In_2Cl_3$, $In_4Cl_7$, and $In_5Cl_9$ have all been reported.[32-36] The interpretation of the vibrational spectra is equally a matter of discussion. Molten $InCl_2$ is shown by Raman spectroscopy to contain $InCl_4^-$ anions,[37] but the room temperature spectrum is variously claimed to show the presence [37] or the absence,[34,35] of this anion in solid $InCl_2$. Six-co-ordination of indium(III) by chloride ions has been reported [35,36] for both $In_2Cl_3$ and $In_5Cl_9$, and again ionic formulations have been proposed for these compounds. In addition, evidence of chemical reactions has been interpreted as supporting both neutral and ionic dimeric formulae for indium dihalides.[4,38-40] Much less attention has been given to indium dibromide and di-iodide than to the dichloride. The Raman spectra now reported clearly demonstrate the presence of the $InX_4^-$ anion (X = Br or I) in the solid state.

Phase studies of the indium–iodine system [41,42] show that only three compounds exist: $InI_3$, $InI_2$, and InI. The Raman spectrum of solid indium di-iodide shows five emissions, readily correlated with the spectrum of the tetrahedral $InI_4^-$ anion: [10,43]

| | | | | |
|---|---|---|---|---|
| $InI_4^-(T_d)$ | 139($\nu_1$) | 42($\nu_2$) | 185($\nu_3$) | 58($\nu_4$) |
| $InI_2$ | 138vs | 47w | 191m, 177mw | 72w, 62 mw $cm^{-1}$ |

It is clear therefore that indium di-iodide can be most simply formulated as $In^I[In^{III}I_4]$, with the $InI_4^-$ anion having a symmetry lower than $T_d$. This structure is in agreement with previous results, which have demonstrated that the high stability of the $InI_4^-$ ion leads to ionic structures in such varying compounds as $[InI_2(dmso)_4][InI_4]$ [$\equiv InI_3,2dmso$ (dmso = dimethyl sulphoxide)] [44] and $[Me_2In][InI_4]$ ($\equiv MeInI_2$).[8] The $InBr{-}InBr_3$ phase diagram [45] requires the existence of $InBr_2$, $In_2Br_3$ and $In_4Br_7$, and $In_5Br_9$ has also been reported; all these species are diamagnetic.[46] The Raman spectrum of $InBr_2$ again correlates well with that [10,47] of $InBr_4^-$:

| | | | | |
|---|---|---|---|---|
| $InBr_4(T_d)$ | 197($\nu_1$) | 55($\nu_2$) | 239($\nu_3$) | 79($\nu_4$) |
| $InBr_2$ | 196vs | 59m | 237w, 227w | 97, 85mw $cm^{-1}$. |

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TABLE 3

Raman spectra (in $cm^{-1}$) of compounds $Me_2bipy,InX_4$

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| X = Cl | | | | | | | | | |
| $InCl_3^{2-}$ | 98w | 102vw | | | | 185m | | | |
| $InCl_5^{2-}$ | | | 104w | 128w | 148w | | 196m | 284m | |
| not assigned | | | | | | | | | 321m |
| X = Br | | | | | | | | | |
| $InBr_3^{2-}$ | 72w | | 106w | 148w | | | | | |
| $InBr_4^-$ | | | | | | 199w | | 237w | |
| X = I | | | | | | | | | |
| $InI_3^{2-}$ | 74w, 79sh | | | 106w | | 136s | | | |
| $InI_4^-$ | | | | | | 136s | 181s | | 196s |

In one experiment, the spectrum showed doubling of the very strong $\nu_1$ emission at 196 $cm^{-1}$, and broadening of the other bands. This could be due to the co-existence of two solid phases; such a phenomenon might explain some of the apparently contradictory results obtained in phase studies of indium–chloride systems. Spectra similar to those given above have recently been reported for $InBr_2$ in the range 190—250 $cm^{-1}$ by Waterworth and Worrall.[48]

The reaction of $Me_2bipy,X_2$ with $InX_2$ (X = Cl, Br, or I) gave in each case a crystalline material of stoicheiometry $Me_2bipy,InX_4$. Table 3 shows the Raman spectra of these compounds. It is clear that in the case of both the bromide and iodide, the spectra can be assigned on the assumption that the solid is an equimolar mixture of $2Me_2bipy^{2+} + In^{I}X_3^{2-} + X^- + InX_4^-$, taking into account the relative intensities of the emissions in question. For the chloride system, the spectrum is made up of the spectra of $InCl_3^{2-}$ and $InCl_5^{2-}$, leaving only one band, that at 321 $cm^{-1}$, unassigned. Again, not all the Raman bands of the two species can be seen because of intensity problems.

These results show that the anionic halide complexes derived from the indium dihalides are, in each case, a diamagnetic mixture of indium(I) and indium(III) species (molar susceptibilities −290 (Cl), −120 (Br), and −445 (I) $\times 10^{-6}$ (c.g.s.u.). These conclusions are in keeping with the formulation of the dihalides as mixed oxidation state compounds, but beyond that can give no information as to the detailed structure. A similar restriction should be applied to all structural conclusions derived from studies of the reactions of indium dihalides, such as leaching experiments with organic solvents. Indium(III) complexes readily undergo rearrangement reactions in non-aqueous solution, and deductions as to structures based only on solution equilibria, conductivity, *etc.*, are therefore often unreliable.[49] It follows that strong reservations must be applied in interpreting the results of studies of non-equilibrium phenomena such as leaching, or chemical reactions in terms of structures in the solid state.

## EXPERIMENTAL

*General.*—Analytical and spectroscopic methods were as in previous work, except that indium analysis was by atomic absorption spectrometry using a Perkin-Elmer 305 instrument. Magnetic measurements were carried out by a conventional Faraday balance method.

*Preparations.*—Indium(III) halides were prepared by the direct reaction of indium metal and the appropriate halogen. The lower halides were obtained by heating a mixture of trihalide and the calculated amount of indium metal for 12—24 h at 250—350° in a sealed tube. In view of the problems encountered by some authors in the identification of the lower halides of indium, the composition of all of these substances were confirmed analytically (Table 4).

*NN'*-Dimethyl-4,4'-bipyridinium halides were prepared following the method described by Michaelis and Hill.[11] After methylation of 4,4'-bipyridyl and isolation of the picrate, the appropriate hydrohalogenic acid was added; the final halide salt was recrystallised from aqueous solution.

TABLE 4

Analytical results for lower indium halides

| | Found (%) | | Required (%) | |
|---|---|---|---|---|
| | In | Halogen | In | Halogen |
| InCl | 76·6 | 23·4 | 76·4 | 23·6 |
| InBr | 58·7 | 41·2 | 59·0 | 41·0 |
| InI | 47·3 | 52·5 | 47·5 | 52·5 |
| $InCl_2$ | 61·7 | 38·6 | 61·8 | 38·2 |
| $InBr_2$ | 42·2 | 58·3 | 41·8 | 58·2 |
| $InI_2$ | 31·3 | 68·9 | 31·1 | 68·9 |

To prepare the indium halide complexes listed in Table 1, a solution of $Me_2bipy,X_2$ in methanol was treated with either a suspension ($In^{I}$, $In^{II}$), or a solution ($In^{III}$) of the indium halide in the same solvent under nitrogen. The mixture was stirred for 2—3 h; removal of solvent *in vacuo* gave the required product.

Unless a trace of halogen was added to the final reaction mixture, the products from the indium(I) and (II) halides were dark blue because of the indicator properties of the cation (see above). The 'bleached' compounds were generally colourless, pale yellow (bromides), or orange-red (iodides).

*Raman Spectroscopy.*—The Raman emission from powdered solids was recorded at room temperature with a Cary 81 spectrometer, using He–Ne excitation.

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