The Lower Oxidation States of Indium

Dennis G. Tuck
Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

1 Introduction

Although interest in the coordination chemistry of the Main Group metallic elements has grown in parallel with the development of transition element chemistry, progress in the former was relatively slow during the years in which rapid advances were made in the latter area, due in part to the lack of experimental and theroetical probes analogous to those provided by ligand field theory, magnetochemistry, and electronic spectroscopy. The structural investigation of colourless diamagnetic compounds depended largely on a mixture of intuition and vibrational spectroscopy until the ready availability of *X*-ray crystallographic methods revealed the real range of preparative and structural problems which challenge the worker in Main Group chemistry.

The availability and sophistication of information on the chemistry of indium typifies this situation. In 1963, it was realistic for D. C. Bradley to summarize what was then known about the stereochemistry of indium in the + 3 oxidation state by stating, simply and correctly, that the coordination number might be either four or six. In the intervening years, a number of review articles have testified to the increasingly sophisticated and detailed information which has become available on the inorganic and coordination chemistry,[1–3] the properties of complexes in solution,[4] and organometallic chemistry,[5] of this element. Even so, most of the published material refers to the chemistry of indium (III), and only in recent years has there been any significant interest in the structure and properties of the oxidation states + 1 and + 2. Again, this situation is similar to that for other Main Group metals, where much of the attention has been on the generally more easily accessible higher oxidation states. The present article reviews the main features of the inorganic and organometallic chemistry of indium(I) and (II), and of the concomitant coordination chemistry, and some possible areas for future development are suggested.

2 The Inorganic Chemistry of Indium(I)

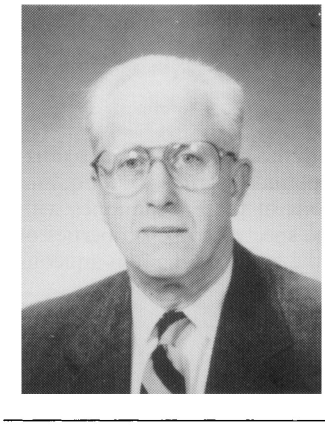
2.1 Binary Halides

A major hindrance to the development of indium(I) chemistry has undoubtedly been the absence of readily available starting materials. The chalcogenides have been known for some time, but have not apparently been useful in synthesis, and the indium(I) halides, although easily prepared, are insoluble in all the commonly available solvents, and in the presence of water or other bases, rapid disproportionation gives indium metal and the corresponding indium(III) species. This reaction

$$3InX \rightarrow In^0 + InX_3 \qquad (1)$$

is a characteristic and all too frequent feature of indium(I) chemistry, and in some circumstances may provide a useful test of the absence of other competing reactions (see below). An interesting feature of the indium(I) halides is that they are generally obtained as coloured solids (red to black, depending on the preparation), which may indicate the presence of either impurities or other oxidation states of the metal. The solid state structures of InBr and InI are both of the TlI type, in which each M^+ ion has X^- neighbours at five of the corners of a distorted octahedron, while InCl has a distorted NaCl lattice.

Professor Dennis Tuck is a graduate of the University of Durham, and much of his early research work was in the field of radiochemistry. Appointments in the University of Nottingham, and Simon Fraser University, preceded a period as Head of the Department of Chemistry and Biochemistry at the University of Windsor, where he now holds the position of University Professor. His present research interests are in Main Group chemistry, in preparative electrochemistry, and in the redox reactions chemistry of Main Group elements. He received the RSC Main Group Chemistry Award in 1986.



Some of the important thermochemical properties of the monohalides are given in Table 1. In view of the later discussion, this Table also contains some important information derived from thermochemical and spectroscopic evidence on the properties of InX molecules in the gas phase, and calculated ΔH_r^0 values for equation 1. The earlier conclusions of Barrow have been recently supported by independent spectroscopic evidence, and it is clear that these molecules are strongly bonded in the gas phase.[4] There is some evidence for dimer formation in the case of InCl.[5]

2.2 Other Indium(I) Compounds

In addition to the binary halides and chalcogenides, a number of indium(I) derivatives of inorganic acids have been prepared. The reaction of cyclopentadienylindium (CpIn, see below) with weak acids results in ligand exchange.

$$CpIn + HL \rightarrow CpH + InL \qquad (2)$$

giving rise to compounds in which L is a singly charged bidentate anion such as quinoline-8-olate. A more general route depends on the method of direct electrochemical synthesis, in which a sacrificial metal anode is oxidized in a non-aqueous solution of a ligand, or ligand precursor, to give the appropriate MX compound.[6] Since the starting point is the metallic element, the technique is especially useful for synthesizing low oxidation species, and indium gives a nice example of this behaviour; for example, the oxidation of indium in the presence of CH_2X_2 (X = Br,I) gives InX as the primary product whose subsequent *in situ* reactions give derivatives such as X_2InCH_2X, $X_3InCH_2PPh_3$, *etc.*[7] In these syntheses, the formation of indium(I) species at the anode can generally be inferred from the number of moles of metal dissolved per Faraday of charge, but the reactivity of these initially formed species is sometimes such that the final product is in fact the corresponding indium(III) compound. It seems probable that these species are formed through electron transfer processes following the electrochemical reactions:

$$\text{cathode: } HL + e \rightarrow L^- + \tfrac{1}{2}H_2 \qquad (3)$$

$$\text{anode: } L^- + In \rightarrow InL + e \qquad (4)$$

$$\text{solution: } InL + HL \rightarrow InL_2 + \tfrac{1}{2}H_2 \qquad (5)$$

$$InL_2 + HL \rightarrow InL_3 + \tfrac{1}{2}H_2 \qquad (6)$$

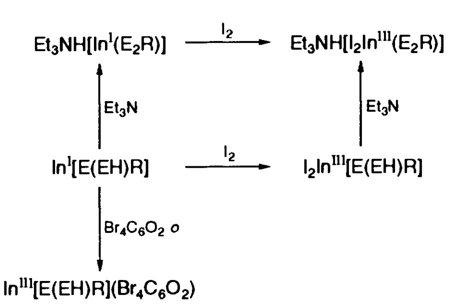
Table 1 Some important properties of indium(I) halides

	M pt/°C	D/kJ mol ^{1a}	r(In–X)(g)/Å^b	$-\Delta H_f^0$/kJ mol ^{1}	ΔH_r^0/kJ [3InX(s) $\rightarrow$ InX$_3$(s) + 2In^0(s)]
InCl	225	428	2 40	186	21
InBr	235	385	2 54	175	96
InI	351	330	2 86	116	110

R F Barrow ref 4(a) ^{b} A H Barrett and M Mandel *Phys Rev* 1955 **99** 666 and refs 4 (b) (c) Values from V V Losev ref 14

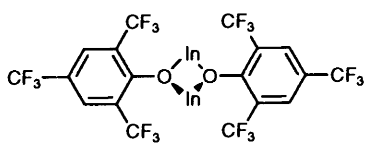
so that InL_3 is the only product recovered from the solution

The electrolytic oxidation of indium into solutions of thiols gives InSR, $In(SR)_2$, or $In(SR)_3$, depending on R, indium(I) species are obtained for R = C_2H_5 or n-C_4H_9, and the stabilizing effect of these groups has been discussed in terms of the charge distribution and its effect on the reactivity of the lone pair of electrons [8] An unusual series of compounds arises from the electrolytic oxidation of indium in solutions of aromatic 1,2-diols, $R(OH)_2$, where the products are of the type $In^I[O(OH)R]$, and with aliphatic dithiols $R(SH)_2$ the similar products are $In^I[S(SH)R]$ [9] The reactions of these substances are very similar, and are summarized in Scheme 1



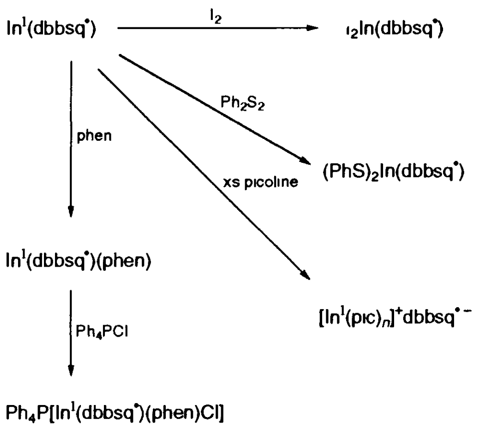
Scheme 1

A related indium(I) compound has been prepared[10] by the reaction of 2,4,6-tris(trifluoromethyl)phenol with InCp to give the dimer (1) in which the two phenyl rings are almost in a plane, and perpendicular to the In_2O_2 ring The average In–O bond distance of 2 320 Å is significantly longer than that in indium(III) complexes It is worth noting that all of the neutral indium(I) species discussed in this section involve ligands which are known to be either chelating or bridging, and it may well be that the acknowledgement that monomeric species will be difficult to prepare is the key to further developments in this area

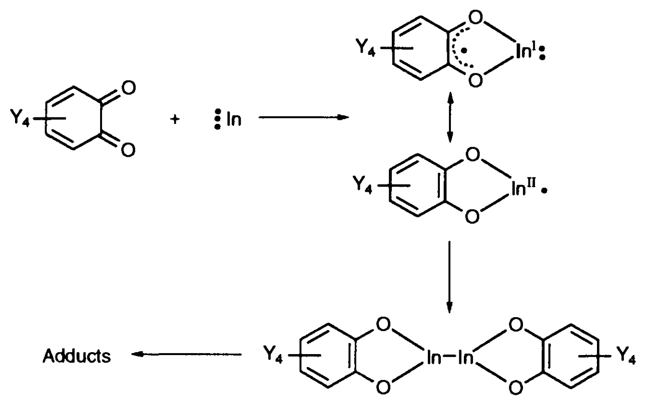


(1)

Another novel indium(I) species which also requires a bidentate ligand can be prepared by direct reaction between equimolar quantities of the element and a solution of 3,5-di-t-butyl-1,2-benzoquinone (dbbq) in refluxing toluene,[11] the product is a solution of the corresponding semiquinone derivative In^I(dbbsq), whose reactions are outlined in Scheme 2 Two important features not normally encountered in Main Group chemistry are the strong colour and the paramagnetic resonance due to the semiquinone ligand, and analysis of the electron spin resonance (ESR) spectrum leads to the hyperfine constant for coupling to ^{115}In (I = 9/2), which is of the order of 9—10 G for In^I, oxidation to In^{III} causes this to drop to ~ 5—7 G, depending on the ligands present, and similar values have been found for other indium(III) species (see below) The energetics of the In/dbbq reaction are obviously an interesting balance of effects, since the analogous reaction between indium and the tetrahalogeno-*o*-benzoquinones ($Y_4C_6O_2$-*o*, Y = Cl,Br) produces derivatives of indium(II) catecholate, formulated as the dimers $(In(O_2C_6Y_4)L)_2$ (L = 1,10-phenanthroline, 4-picoline) [12] The ESR evidence shows the presence of semiquinone species in the reaction media, and hence the initial reactions are presumably those shown in Scheme 3, rather than the reaction shown in equation 7



Scheme 2



Scheme 3

$$In + dbbq \rightarrow In(dbbsq) \qquad (7)$$

Such differences are in keeping with the known stronger oxidizing power of the $Y_4C_6O_2$-*o* compounds relative to dbbq, and parallel that found in the reactions of these *o*-quinones with indium(I) halides (see below) The spectroscopic properties of In(dbbsq) make it attractive for the study of the non-aqueous solution chemistry of indium(I)

2.3 Indium (I) Complexes

Much of the chemistry of indium(I) is concerned with its oxidation reactions, in which electrons are lost, but there are also a number of species which show that indium(I) compounds can act as electron pair acceptors, these will be briefly treated in the order neutral, cationic, and anionic.

Indium(I) halides are reported to form ammine complexes InX·nNH$_3$ (n = 1,2) which disproportionate upon heating to In, NH$_3$, and InX$_3$·yNH$_3$. Adducts with aniline and morpholine, of the type [InL$_4$]X and [InL$_2$]X (X = Cl,Br,I), have also been identified, but in neither study was structural characterization possible,[1] while adducts of In$^{\rm I}$(dbbsq) within 1,10-phenanthroline were isolated in studies of that compound.[11] Solutions of indium(I) halides in mixtures of aromatic solvents and organic bases yield solid adducts of the formula InX·0.5tmen (X = Br, I, tmen = *N,N,N′,N′*-tetramethylethanediamine), although this does not appear to be the predominant solution phase species.[13] To summarize, a small number of adducts with nitrogen bases are known, but no structural information is available, due in part to the inherent instability of such compounds towards disproportionation, which occurs readily, and in some cases with explosive violence, in the presence of donor ligands. The calculated enthalpy change for the parent InX/InX$_3$ systems is positive for X = Cl, Br, or I (Table 1), so that the instability of the adducts of InX is presumably enhanced by the enthalpy of complexation of InX$_3$. As in much of this area of chemistry, detailed analysis is impossible because of the lack of thermodynamic data, but it seems safe to conclude that stable adducts of InX with hard donor ligands will be difficult, if not impossible, to prepare because of the stability of the corresponding indium(III) species, and soft ligands may offer a better reward in this context.

Cationic complexes of indium(I) can be obtained by using In$^{\rm I}$[In$^{\rm III}$X$_4$] [X = Cl, Br, I) or similar species as starting materials, the structure of these indium(II) compounds is discussed below (Section 6.1), but for the moment it is sufficient to note the presence of In$^+$ cations in the solid state. Prolonged treatment with either 6,7,9,10,17,18,20,21-octahydrodibenzo(*b,k*)-[1,4,7,10,13,16]hexaoxacyclo-octadecane(dibenzo-18-crown-6) or 1,4,8,11-tetraazacyclotetradecane (cyclam) yielded [InL)InX$_4$ (L = crown ether or cyclam, X = Cl, Br, I), and similarly InAlCl$_4$ gave [InL]AlCl$_4$. These are complexes of the In$^+$ cation, stable in the solid state but decomposing in common organic solvents by loss of ligand and deposition of InX. Similar compounds were identified in the In$^{\rm I}$(dbbsq$^-$) system, where the addition of a large (~ 100-fold) excess of 4-picoline gave a solution of free dbbsq$^-$ and a cation presumed to be [In(pic)$_n$]$^+$. The study of these cationic complexes has been hindered by the absence of starting materials other than In$_2$X$_4$. It seems clear that the stabilization of In$^+$ as [InL$_n$]$^+$ is helped by the suppression of disproportionation, in the case of L = crown ether or cyclam, the corresponding indium(III) cationic complex is unlikely to be stable, and decomposition in fact yields InX and InX$_3$·L (see below). Given the range of multidentate complexing agents now available, it should be possible to design a system in which the balance of complexation and lattice forces will allow the stabilization of salts of crystalline In$^+$ species. The stabilization of In$^+$ in aromatic solvents is discussed below (Section 2.5.2).

Both simple and complex anionic indium(I) derivatives are known. The treatment of InX with [bpyMe$_2$-4,4′]$^{2+}$(X$^-$)$_2$ gives salts of InX$_3^{2-}$, isoelectronic with SnX$_3^-$, and formulated as mononuclear C_{3v} species on the evidence of vibrational spectroscopy. The related [NEt$_4$][InX$_2$] salts can be prepared by the reaction

$$\mathrm{InCp + NEt_4X + HX \rightarrow CpH + [NEt_4][InX_2]} \qquad (8)$$

for X = Cl, Br, or I, and the iodo species can also be obtained electrochemically. Metathesis yields the corresponding [In(NCO)$_2$]$^-$ and [In(NCS)$_2$]$^-$, and [In(NCS)$_3$]$^{2-}$ has also been prepared, but none of these apparently simple species has been structurally characterized. The ease of preparation and the apparent stability is probably aided by the fact that the disproportionation

$$\mathrm{3InX_2 \rightarrow InX_6^{3-} + 2In^0} \qquad (9)$$

is hindered by a high energy of activation.

More complicated anions have also been prepared. The complexes I[O(OH)R] and In[S(SH)R] both involve anions with an -OH or -SH group on the ligand, and treatment of these with NEt$_3$ results in proton transfer to give the salts (*e.g.*) [NEt$_3$H]$^+$ [InS$_2$R]$^-$ in which the oxidation state of the metal has been confirmed by reaction with I$_2$. The coordination number of indium(I) in such anions is not known, but it seems unlikely that these are simple mononuclear complexes. Another anion is [In(dbbsq$^-$)(Cl)phen]$^-$, stabilized as the PPh$_4^+$ salt, and in general it seems likely that a series of anionic complexes with different mono- or bidentate ligands could be prepared as stable molecules, so that the full range of accessible structures could be established. The question of the stereochemical effect of the 'lone pair' of electrons in indium(I) complexes could then be properly addressed.

2.4 Solution Chemistry

Given the ready disproportionation of indium(I) compounds in the presence of donor ligands, it is not surprising that there have been few studies of the behaviour of this state in aqueous solution. The electrochemical aspects of the problem have been discussed by Losev.[14] Despite the experimental difficulties, In$^+$(aq) species have been generated by the *in situ* reduction of the metal, and the kinetics of their oxidation by Fe$^{\rm III}$ investigated. The kinetics of the disproportionation process have been used to derive stability constants for In$^+$/X$^-$ systems,[2] for which

X = F, $\log\beta_2$ = 2.46
Cl, $\log K_1$ = 2.37
Br, $\log K_1$ = 1.56
$\log\beta_2$ = 2.11

Not surprisingly, these tentative values imply only weak formation of the InX$_2$ in aqueous media.

Despite the fact that disproportionation is enhanced by basic ligands, indium(I) halides are soluble in mixtures of aromatic solvents and bases. The original studies[13] involved toluene/tmen mixtures, in which InBr and InI form solutions whose stability against disproportionation depends on the temperature. At −20 °C, the solubility of InBr also depends on the concentration of tmen, reaching a maximum of 15.7 ± 0.02 mmol dm^{-3} (3.06 mg cm^{-3}) when [tmen] = 0.15 mol dm^{-3}. The dependence on [tmen] at low concentrations implies that the solution species is InBr·3tmen, but addition of light petroleum in this solution precipitated InBr·0.5tmen. When the temperature was allowed to rise above 0 °C, disproportionation to 2In^0 + InX$_3$L$_n$ occurred, giving products whose nature depended on the properties of the base L. The nature of the solute species is unclear, other than the obvious fact that coordination (*i.e.*, solvation) by tmen or other bases is crucial, as is the presence of an aromatic, as opposed to any other hydrocarbon, solvent, but the degree of association of the solute has not been established. The rich variety of structures that has been identified in compounds of (say) lithium with organic bases suggests that it would be unwise to speculate on the basis of stoichiometry alone. The main advantage of these solutions is that they allow the study of a number of oxidative processes which might otherwise be inaccessible.

2.5 Cyclopentadienylindium (I) and Analogues

2.5.1 Preparation and Structural

At several points the absence of readily available inorganic indium(I) compounds has been emphasized, and the consequent problems have made the existence of cyclopentadienylindium(I) a welcome fact of life. This compound was first prepared by Fischer and Hofmann,[15] in a reaction between InCl$_3$ and excess NaCp, InCp is obtained by sublimation, together with trace amounts of InCp$_3$. Later experiments showed that substituting

LiCp for the more reducing NaCp enhances the formation of $InCp_3$, and the production of InCp in the original reaction may be due to the reduction of $InCp_3$ Methylcyclopentadienylindium(I) was also prepared *via* $In(MeCp)_3$, but the indenyl analogue could not be isolated A more convenient synthesis of InCp involves the metathesis of LiCp and InCl in diethyl ether,[16] and another route[17] involves the co-condensation of metal vapour and CpH at 77 K The substance is sensitive to oxygen, but unaffected by water, InMeCp is much more air-sensitive

The chemistry of this fascinating molecule is a direct reflection of its structure, although that structure itself raises some challenging questions The structure of crystalline InCp is that of a linear homopolymer, with each indium atom lying between two C_5H_5 rings, on the ring C_5 axis, with r(In–centre) = 3 19(10) Å This form of packing is in keeping with the substantial dipole moment, but an unusual feature is that although the rings are orthogonal to the In–In axis, there is an angle of 137 ° at centre–In–centre The inter-chain In–In distance is 3 99 Å, which is long compared to the In–In bond distance of 2 775(2) Å in In_2Br_3I 2tmen (see below) The structure of InCp in the gas phase, determined by electron diffraction, is that of a half-sandwich, with C_{5v} symmetry (r(In–C) = 2 621(5) Å and r(C–C) = 1 427(7) Å), the hydrogen atoms of the C_5H_5 ring are bent away from the metal by 4 5 ° The bonding in this molecule is covalent, not ionic, and early CNDO calculations provided a description involving the interaction of the p_π orbitals of the ring-carbon atoms with both a hybrid sp orbital and the p_x and p_y orbitals of the metal, and also correctly predicted the presence of a large dipole moment (calcd 4 75 D, found 2 2 D at 40 °C in toluene), which was identified with the existence of a metal-atom lone pair of electrons perpendicular to the ring Two photoelectron spectroscopic investigations[18 19] of InCp are in substantial agreement with each other, but sophisticated SCF methods[20 21] were required to obtain an MO scheme in agreement with the spectroscopic results In this treatment, the HOMO is a doubly degenerate MO formed from the e p_π orbital of C_5H_5 and p_x and p_y of In The lone pair, which is an important feature of the chemistry of InC_5H_5, is then the next highest orbital involving indium $5s$ (or $5s + 5p_z$) interacting with the a_1 ligand π-orbital It is worth emphasizing that either oxidation or complexation (see below) causes a change in hapticity from five to one, so that any alteration in the electron density at the metal, and especially in the lone pair, has concomitant effects on the metal–ligand interactions, apparently destroying the π-interactions which are critically important in the η^5-bonding mode

Our knowledge of the structural behaviour of organoindium(I) compounds has recently been considerably enhanced by the work of Beachley and his colleagues,[22] who have prepared and structurally characterized crystalline $In(C_5Me_5)$, $In(C_5H_4Me)$, $In(C_5,H_4SiMe_3)$, and $In(C_5H_4Bu^t)$ A related member of this series is $In[C_5(CH_2Ph)_5]$ [23] Electron diffraction results have also been reported for $In(C_5Me_5]$ and $In(C_5H_4Me)$ The predominant feature is still the half-sandwich structure, with the indium situated on a C_5 axis, but there are fascinating differences in the ways in which these molecules pack together in the solid state The zig-zag homopolymeric form of $In(C_5H_5)$ has been confirmed, and this structure is also found for $In(C_5H_4Me)$, in both cases In–In distances of 3 986(1) Å are observed The zig-zag infinite chains are also found in $In(C_5H_4SiMe_3)$ and $In(C_5H_4Bu^t)$, but in these cases there are no close In–In contacts Finally $In[C_5(CH_2Ph)_5]$ is a quasi-dimer,[23] with In–In contacts of 3 631 Å, while $In(C_5Me_5)$ in the solid state forms a hexamer in which indium atoms are at the corners of an octahedron, with the C_5Me_5 rings on the outside, one important detail is that vectors from the centres of the rings through the indium atoms do not point at the centre of the octahedron The main structural features of these molecules have been summarized by Beachley [22e]

In addition to the question of the molecular structure and bonding in these compounds, the *X*-ray results reveal a series of challenging intermolecular arrangements, which have prompted much discussion Dimer formation has been discussed in terms of In–In interactions involving lone-pair → p_π donation [24] A much more detailed analysis of M–M bonding (M = In,Tl) has been given by Janiak and Hoffman,[25] who emphasize the importance of considering both metal and ligand in solid-state packing Their treatment leads to a rational explanation of the intermolecular interactions in InCp and its congeners Perhaps the most important theme of this long and important paper is that the structural chemistry of organoindium(I) and related compounds is too subtle to be treated by simplistic arguments

Until recently, InCp and its derivatives were the only stable organoindium(I) compounds known, but Cowley[26] has recently reported the synthesis of $[(Me_3Si)_3C]In$ by the metathesis of the lithio compound and InCl The crystal structure unfortunately did not refine, but indicates the presence of a tetrameric unit with indium atoms at the corners of a tetrahedron, (r(In–In) ~ 3 0 Å)

2 5 2 Indium(I) Arene Solvates

Organotransition metal chemists have brought order into their work by organizing ligands in terms of the number of electrons which each may contribute to the 18-electron formalism This scheme has not been widely used in Main Group chemistry, which is surprising, because it can lead to useful rationalizations A case in point is InCp, which is an 18-electron system if one counts $4d^{10} + 4s^2 + 5p^1 + 5(Cp)$, a simpler and equally useful formalism is the EAN rule, 49 + 5 = 54 (Xe) Such an approach emphasizes the bonding relationship between InCp and (say) CpSnCl, and between cyclopentadienyl compounds and arene solvates

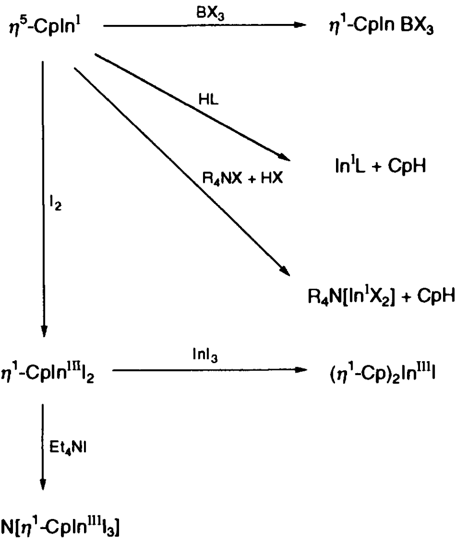
The solubility of In_2X_4(and Ga_2X_4) compounds (see Section 6 1) in aromatic solvents is in sharp contrast to the insolubility in other hydrocarbons This has been correctly attributed to the formation of $[M(arene)_n]^+ MX_4^-$ solute species, and in recent years stable crystalline derivatives have been obtained Given the complexity of the solid state chemistry of the cyclopentadienyl derivatives discussed above, it is not surprising that there are some challenging problems in this area

The only indium(I) compound studied crystallographically is $[(1,3,5\text{-}Me_3C_6H_3)_2In]InBr_4$, in which In^+ is coordinated by two η^6-arene units, whose planes are at an angle of 47 3 °, two bromine atoms from the pseudo-tetrahedral $InBr_4^-$ anion are also in the coordination shell Such compounds are only formed with substituted benzenes Similar bis-arene complexes have been reported with Ga_2X_4, but here there is also a mono-η^6-arene species, $[(Me_6C_6)Ga]GaBr_4$, in which Ga^I resides on the six-fold axis of the C_6 ring, and this despite the (so far) non-existence of Ga^ICp or derivatives No doubt in this area, as with the C_5 compounds, a complex set of solid state and bonding interactions awaits elucidation

2 5 3 The Reactions of Organoindium(I) Compounds

While there can be little doubt as to the reality of the structural problems outlined in Section 3 1, there is equally no doubt that the reactions of InCp, and of other indium(I) species, can be rationally discussed by acknowledging the presence of an available pair of electrons Regardless of whether or not these constitute a stereochemically active lone pair, they do behave as a reactive lone pair, and this is implicitly accepted in the remainder of this review

In addition to the oxidation processes discussed in detail below, the lone pair gives InCp Lewis-base properties, so that the compound forms adducts with BX_3 (X = F,Cl,Br,Me), and in so doing, according to the infrared evidence, changes to η^1-$C_5H_5In\ BX_3$ This change is in keeping with the MO schemes discussed above, since the donation of electron density results in the destabilization of the M-ring interaction It also follows that other organoindium(I) compounds should have some Lewis-base activity, although no direct evidence of this has been reported The use of InCp in metathetical reactions was discussed earlier, and these and other processes are summarized in Scheme 4.



Scheme 4

Beachley *et al.* have used the acid hydrolysis of In^IR species as a means of characterization

$$InR + 3H^+ \rightarrow In^{3+}(aq) + H_2(g) + RH \qquad (10)$$

but in each case the yield of H_2 is *ca.* 95% of theoretical, suggesting that the process may go *via*

$$InR + H^+ \rightarrow In^+(aq) + RH \qquad (11)$$

$$In^+(aq) + 2H_2O \rightarrow In(OH)_3(aq) + H^+ + H_2 \qquad (12)$$

$$In(OH)_3(aq) + 3H^+ \rightarrow In^{3+}(aq) + 3H_2O \qquad (13)$$

in which case, there will be a competing disproportionation

$$3In^+(aq) \rightarrow In^{3+}(aq) + 2In^0 \qquad (14)$$

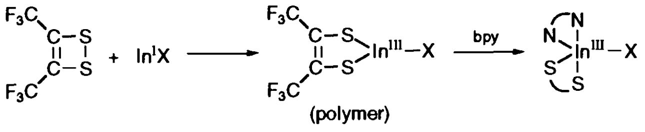
which is related to equations 1 and 9. The deposition of indium metal during the hydrolysis is in agreement with this.

2.6 Oxidation Reactions of Indium(I) Compounds

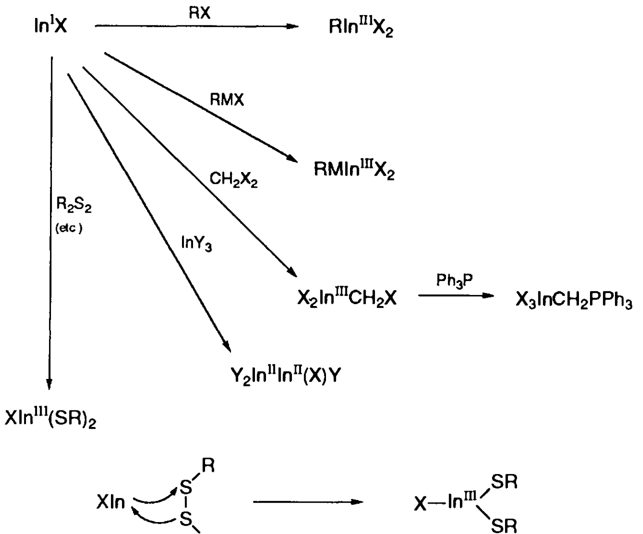
Not surprisingly, a characteristic reaction of indium(I) compounds is oxidation to either indium(II) or (III). The simplest of these is oxidation by iodine (see Schemes 1, 2, and 4) to give the corresponding $XInI_2$ compounds, and this reaction produces readily identifiable indium(III) complexes under the appropriate conditions. We should note that in the case of InCp, these indium(III) species all involve η^1-ligation, again emphasizing the importance of the available pair of electrons in stabilizing the η^5-mode of bonding.

An important class of reactions is that involving oxidative addition of InX to various substrates. Despite the view that such reactions lie exclusively in the domain of organo–transition metal chemistry, there is ample evidence of oxidative addition (or insertion) with many low oxidation state Main Group inorganic and organometallic compounds (using the term without prejudice as to the detailed mechanism of the reaction). The reaction of InBr or InI with the corresponding RX (R = Me, Et, n-Bu, t-Bu, allyl, CH_2Ph) gives $RInX_2$ in good yield at rates which depend markedly on the nature of R and X. A mechanism which supposes the participation of various indium sub-halides has been proposed, but the evidence for this is indirect, and research is needed to establish the mechanism, since radical species may be invoked (*cf.* *o*-quinone oxidations below). The reactions are very useful methods for the preparation of organoindium(III) halides.

A related reaction involves the insertion of In^I into E−E bonds, an early example being the opening of the S−S bonds of the dithiete ring by InX (X = Cl,Br,I) or InCp (Scheme 5) to produce InS_2C_2 ring systems with typical indium(III) coordination chemistry. These heterogeneous reactions of InX were later extended[13] by using InX/toluene/tmen solutions with Ph_2S_2, Ph_2Se_2, $PhCO_2O_2CPh$ or $Co_2(CO)_8$, in which case the products were (*e.g.*) $XIn(SPh)_2$, isolated as adducts with monodentate donors (Scheme 6), although a number of substrates, including Ph_4P_2, Ph_6Pb_2, 2,4-dinitrophenylhydrazine, $Mn_2(CO)_{10}$ and $[(C_5H_5)Fe(CO)_2]_2$, failed to react under these conditions. In related studies, Ph_3SnX (X = Cl,Br,I) or Ph_3SnOAc gave Ph_3SnInX_2 tmen (*etc.*) as the product, but again no reaction was detected with Me_3SnCl, Ph_3SnH, Ph_3GeCl, Ph_3PbCl, or Ph_2PCl.[28] It is possible to rationalize these results by a model in which the transfer of electrons is accounted for without allowing any inference about the detailed mechanism, and which presumes that the substrate must have both donor and acceptor properties. Given the significance of one-electron transfer in other oxidation processes with InX, it is also possible that a free radical mechanism would equally well explain the results, and this is being explored.



Scheme 5



Scheme 6

Two other oxidation reactions lend themselves to explanation *via* an oxidative addition mechanism. When InX (X = Cl,Br,I) is refluxed with pentane-2,4-dione (Hacac), the product is a mixture of $In(acac)_3$ and $InX_2(acac)$, the latter being isolated as the adduct $InX_2(acac)L$ (L = bpy, *etc.*). Similarly, In^I[qno = quinoline-8-ato anion) and excess Hqno yielded $In(qno)_3$, while with Hacac the product was $In(qno)(acac)_2$. The reactions can be seen as the result of the reactions

$$InL + HL \rightarrow HInL_2 \qquad (15)$$

$$HInL_2 \rightarrow H + InL_2 \qquad (16)$$

$$2InL_2 \rightarrow InL_3 + InL \qquad (17)$$

followed by elimination of hydrogen ($2H \rightarrow \frac{1}{2}H_2$) and the dimerization and disproportionation of the resultant indium(II) species, probably *via* the mechanism discussed below. This is in keeping with the *in situ* conversion of electrochemically produced In$^{\mathrm{I}}$ species by similar processes in the presence of excess HL (see Section 2.2).

2.7 General Conclusions

It will be clear from the review of the inorganic chemistry, coordination chemistry, and organometallic chemistry of indium(I) that this is in fact a well-established area of Main Group chemistry, and merits something more than the cursory treatment which it normally receives in textbooks. The redox chemistry is an area full of promise, both in the scope of the reactions which can be studied, and the mechanistic problems which need to be unravelled. Much the same comments can be made about the low oxidation state chemistry of a number of the other heavier *p*-block elements, and there is much to be done to understand the details of the structures and reactions involved.

3 Indium(II) Chemistry

3.1 Indium(II) Halides

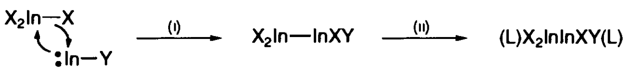
The structure of the crystalline indium dihalides, stoichiometry InX_2($X = Cl,Br,I$), is a classical problem in Main Group chemistry, as is that of the analogous gallium compounds. The bromide and compounds can be readily obtained by controlled halogenation of the metal, by reduction of InX_3 by the metal, or by the reaction of InX with InX_3. The chloride is not accessible by these reactions, and there is considerable doubt about the very existence of this compound. There is a long history to this matter, in which phase studies have played a part, that has been reviewed elsewhere[1,29] as has the question of the other subhalides such as In_2Cl_3, In_4X_7 and In_7Br_9.[25]

Since the dihalides are all diamagnetic they cannot be monomers, as the In^{2+} ion must be paramagnetic, leading to the postulation of either X_2InInX_2 or $In^{I}[In^{III}X_4]$ structures. It is important to stress here that simplistic but nevertheless credible arguments show that the M–X bonds in a mononuclear MX_2 molecule should be reasonably strong, so that the non-existence of such species must be ascribed to the kinetic reactivity of the unpaired electron rather than to any thermodynamic instability. There is a challenging problem in the possible stabilization of a stable complex of monomeric InX_2 in a structure which would minimize this reactivity by appropriate electronic and steric effects.

For crystalline In_2I_4 the structure has been shown by *X*-ray crystallography to be built up from InI_4^- tetrahedra which are organized around the In^+ cation to give eight-fold coordination of the latter by iodine. The structure of In_2Br_4 is apparently similar, since Raman spectroscopy establishes the presence of $InBr_4^-$ in the solid state. The solubility of those compounds in aromatic hydrocarbons due to solvation was discussed earlier. The apparent non-existence of $InCl_2$, coupled with the existence of In_2Cl_3, In_5Cl_9, and In_7Cl_9, can be perhaps understood in the following way. Indium(III) is six-coordinate in crystalline $InCl_3$, and this appears to be the most stable coordination state with chloride ligands, since $InCl_6^{3-}$ is the most readily formed anionic complex, $InCl_5^{2-}$ and $InCl_4^-$ are only found in salts with large organic cations. It is therefore not unreasonable that In^{I}[$In^{III}Cl_4^-$] should not be a stable lattice, and that the simplest mixed-oxidation state crystalline solid is $In_3^{I}[In^{III}Cl_6]$, which is in fact found for In_2Cl_3, Similarly, In_3Cl_9 can be written as $In_3^{I}[In_2^{III}Cl_9]$, again containing six-coordinate indium(III), while the recently reported In_7Cl_9 can be described as a derivative of InCl, with In^{III} appropriately substituted into the lattice. As in so many other cases, *X*-ray crystallography has illuminated a formerly murky area of Main Group chemistry. A similar clarification of the species present in molten indium dihalides would be equally welcome. There is, in summary, no evidence for In–In bonding in any of these halides in the solid state.

3.2 Complexes of Indium(II) Halides

Neutral adducts of In_2X_4 can be prepared either by treating the dihalide with a range of neutral donors at low temperatures, or by the oxidative insertion of InY into an X_2In-X bond in the presence of a donor.

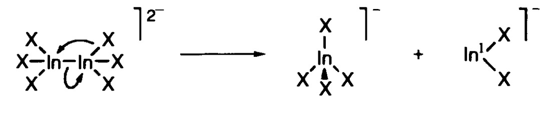


(18)

Anionic derivatives $In_2X_6^{2-}$ have been obtained by treating In_2X_4 with $2R_4NX$ in aromatic solvents. These anions are stable in the solid state, but ^{115}In NMR spectroscopy showed that disproportionation occurs in non-aqueous solution.

$$In_2X_6^{2-} \rightleftarrows InX_4^- + InX_2^- \qquad (19)$$

and this process is obviously the inverse of equation 18(i).

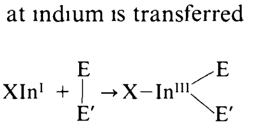


(20)

The only structural information on these anions comes from vibrational spectroscopy, but the analogous gallium(II) species are certainly based on M–M bonding, and there is no reason to doubt the validity of the proposed structure. It has been argued elsewhere[31] that the stability of these neutral and anionic In–In bonded molecules depends not so much on the strength or weakness of the In–In bond, whose dissociation energy is estimated to be of the order of 85 kJ mol^{-1}, but rather on the ease of halide transfer between the two metal centres (*i.e.*, the inverse of equation 18(i), or the analogue of equation 20). It follows that while uncoordinated $X_2In-InX_2$ species do not exist in the solid state for X = halide, it should be possible to prepare similar molecules if X is a poor leaving group, and in keeping with this argument, $[(Me_3Si)_2CH]_2InIn[CH(SiMe_3)_2]_2$ has been prepared and characterized,[32] the In–In bond distance is 2.828(1) Å, and r(In–C) = 2.19(1) Å, and the coordination at indium is almost planar trigonal. Similar distances are found in $(R_F)_2InIn(R_F)_2$ (R_F = 2,4,6-$(CF_3)_3C_6H_2$), for which r(In–In) = 2.744(2) Å and r(In–C)(av) = 2.22 Å, this latter molecule also shows evidence of intramolecular In–F interactions.[33] Stabilization by adduct formation stabilizes the In–In structure in a similar way, since halide transfer is prevented by blocking the metal through coordinative saturation to give the anionic or neutral derivatives noted above. One of the latter, In_2Br_3I·2tmen, has two five-coordinate indium(II) centres linked through an In–In bond for which r(In–In) = 2.775(2) Å.[34] As with other topics discussed in this review, there is no reason to suppose that further In–In species cannot be prepared, given careful choice of ligands. Thermochemical measurement of the dissociation energy of this bond would be especially welcome. We should also note that the chemistry of Sn–Sn bonded Sn_2L_6 species shows somewhat analogous behaviour, in that the halide species are unstable against disproportionation while the organic compounds are reasonably stable, and it may well be that the conclusions about the intramolecular mechanism of dissociation are of general application in Main Group chemistry.

4 Electron Transfer Processes in Indium Chemistry

The oxidation of various indium(I) species has been discussed in earlier sections, with the general conclusion that these processes could be viewed as addition reactions in which the pair of electrons at indium is transferred.



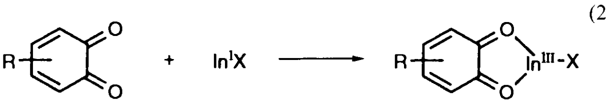
$$XIn^{I} + \begin{matrix}E\\|\\E'\end{matrix} \rightarrow X\text{–}In^{III}\begin{matrix}\diagup E\\ \diagdown E'\end{matrix} \qquad (21)$$

This equation is parallel to that written for association in the system

$$PCl_3 + Cl_2 \rightleftarrows PCl_5 \qquad (22)$$

but the reverse processes, the reductive elimination reactions of InX_3 species, are unknown (with the possible exception of the thermal decomposition of $InCp_3$ to InCp) Despite the ready acceptance of equations such as 22, which can be found in every elementary textbook, there is essentially no evidence as to the mechanism in the case of Main Group compounds, and the assumption that a pair of electrons is transferred in some concerted fashion seems to have been based on the lack of anything better

A few years ago, in the course of investigating such reactions with indium(I) halides, we examined their oxidation by substituted *o*-quinones, and in particular $Y_4C_6O_2$-*o* (Y = Cl,Br) and 3,5-di-tert-butyl-*o*-benzoquinone (dbbc)[35] We found the expected formation of the indium(III) halide–catecholate complex



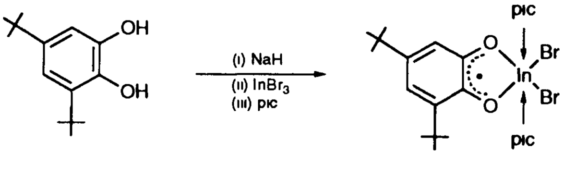
(23)

whose coordination and structural chemistry showed all the established features of an indium(III) compound Such reactions are in fact common to other low oxidation state complexes of the *p*-block elements, and we have subsequently studied similar reactions with TlX, GeX_2, SnX_2, PbX_2, PR_3, SbR_3, and TeR_2 compounds In each case, electron spin resonance (ESR) spectroscopy has shown the formation of an intermediate in which the *o*-semiquinonate ligand is attached to the central element, the ESR spectrum typically contains the characteristic free-radical spectrum with evidence of coupling to the *p*-block element[36]

The indium case was one of the first to be investigated in detail, and the reaction pathway has been explained in terms of indium(I) (II), and (III) species in the solution phase The first step in the reaction between InX and a quinone Q is presumed to be a one-electron transfer (*cf* Scheme 3)

$$InX + Q \rightarrow XIn\,(SQ\ ) \qquad (24)$$

and the subsequent reactions of this indium(II) diradical species depend essentially on the unpaired electron at indium, and not that on the radical–anion ligand, so that here, as in the corresponding SnX_2/Q reaction, addition of $\frac{1}{2}I_2$ produces XInI(SQ) Such species would be expected to be thermodynamically stable (see above), and in fact it proved possible to synthesize an indium(III)–semiquinone compound by the route



(25)

where pic = 4-methylpyridine The molecular structure of this adduct was established by *X*-ray crystallography, and proved to be that of a six-coordinate indium(III) compound, with an $InO_2N_2Br_2$ kernel, and the *X*-ray results identified the C–O bond distance in the SQ ligand as 1 28(2)Å, which is close to the generally accepted value for *o*-semiquinones The ESR spectrum of the molecule was also in agreement with this formulation, and in particular yielded a hyperfine coupling constant $A_{In} \sim 6$ G, significantly lower than that for In^I(SQ) (see Section 2 2)

The ESR spectrum of the InX/Q reaction mixture shows that both indium(I) and indium(III)-semiquinone species are present, and while there are some important unresolved details in the explanation of these results, the overall scheme is essentially that shown in Scheme 7 A key step is the dimerization of the XIn (SQ) units to give an In–In bonded molecule, which disproportionates by the halide transfer process discussed above to give In^I(SQ) and $In^{III}X_2$(SQ) For the most strongly oxidizing $Y_4C_6O_2$-*o*, these intermediate species cannot be identified and the final products are derivatives of $In^{III}(Y_4C_6O_2]X_2$

$$\begin{tikzcd}
Q + In^I \arrow[r] & (SQ^{\bullet})\dot{I}n^{II}X \arrow[r, "1/2\ I_2"] \arrow[d] & (SQ^{\bullet})In^{III}(X)I \arrow[d, "L"] \\
& (SQ^{\bullet})XIn^{II}In^{II}X(SQ^{\bullet}) \arrow[d, shift left] & (SQ^{\bullet})In^{III}(X)IL_n \\
& (SQ^{\bullet})In^I + (SQ^{\bullet})In^{III}X_2 \arrow[u, shift left] \arrow[r, "L"] & (SQ^{\bullet})In^{III}X_2L_n
\end{tikzcd}$$

Scheme 7

It is satisfying to find that these interesting systems can be understood in terms of the known coordination chemistry of indium in each of its oxidation states Furthermore, such reactions are apparently typical of the *p*-block elements – for example, the reactions of SnX_2 closely parallel those just described, and the Sn–Sn bonded diradical can be identified from the ESR spectrum – and two important questions then arise about the proposed mechanism The first is why such one-electron processes have not been previously postulated in Main Group redox chemistry, and the answer to this is probably that most of the two-electron oxidants used (*e g* halogen) react so rapidly that the spectroscopic identification of the one-electron intermediate is impossible by present techniques The second, which follows in part from this conclusion, is whether one can identify hitherto unexplored oxidation reactions in which radical intermediates might be involved One possible system which is presently being investigated involves the reaction

$$InX + RX \rightarrow RInX_2 \qquad (26)$$

which has been known for several years (see Section 2 6) A possible initial step in a reaction scheme based on one-electron transfer is

$$XIn\ + R{-}X \rightarrow X_2In\ + R \qquad (27)$$

and in fact it has already been suggested from the synthetic work that low oxidation indium species are involved These could obviously be formed by

$$2X_2In\ \rightarrow In_2X_4 \qquad (28)$$

and one obvious confirmation of the scheme would be by direct identification of the organic radical R Other reactions in Scheme 6 also offer interesting possibilities for mechanistic investigations

5 Postlude

The chemistry of indium exemplifies much that is valid for other Main Group elements – the coordination chemistry of the higher oxidation states still retains, from a distance, a deceptive air of simplicity, while the chemistry of the lower oxidation states is largely unexplored Perhaps the best advice to the prospective researcher is to ignore the generalized and comforting indications found in some textbooks to the effect that this is a tranquil region, lacking in challenge, and to explore instead the many topics which merit the attention of modern inorganic and organometallic chemists

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