Coordination compounds of indium. Part 39. Some neutral adducts of In₂Br₄ and In₂I₄

MICHAEL J. TAYLOR,[1] DENNIS G. TUCK,[2] AND LUIS VICTORIANO

Department of Chemistry, University of Windsor, Windsor, Ont., Canada N9B 3P4

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The neutral indium(II) compounds $In_2X_4(Et_3P)_2$, $In_2X_4(TMED)_2$, and $In_2X_4(TMED)_2C_6H_6$ (X = Br, I; TMED = N,N,N',N'-tetramethylethylenediamine) have been prepared by the reaction of InX_2 and donor in benzene or toluene. With several other neutral donors, and in all systems involving $InCl_2$, decomposition to In^0 is the predominant process. Analysis of the vibrational spectra demonstrates that these structures involve $X_2In–InX_2$ kernels. Slight revisions are proposed to previous discussions of the infrared spectra of $In_2X_6^{2-}$ anions.

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On a préparé les composés neutres de l'indium(II) $In_2X_4(Et_3P)_2$, $In_2X_4(TMED)_2$ et $In_2X_4(THED)_2 C_6H_6$ (X = Br, I; TMED = N,N,N',N'-tétraméthyléthylènediamine) en faisant réagir InX_2 avec un donneur dans le benzène ou le toluène. La décomposition en In^0 est la réaction principale avec plusieurs autres donneurs neutres et dans tous les systèmes qui impliquent $InCl_2$. L'analyse des spectres de vibration démontre que ces structures font intervenir les noyaux $X_2In–InX_2$. On propose une légère revision des discussion antérieures des spectres infrarouges des anions $In_2X_6^{2-}$.

[Traduit par le journal]

Introduction

In a number of previous publications from this laboratory we have commented on the dearth of information on the chemistry of the lower oxidation states of indium. Recent papers have described the development of synthetic routes to a number of neutral (1), cationic (2), and anionic (3) complexes of indium(I) and there does not seem to exist any barrier now, in principle, to the extension of such work to related systems. On the other hand, the chemistry of indium(II) still presents a number of challenging problems. The neutral dihalides are generally formulated as ionic dimers of mixed oxidation state, and a simple route to the preparation of these compounds (4) also lead to the development of synthetic routes to the first anionic complexes $In_2X_6^{2-}$ (5). These anionic species are structurally similar to the digallium salts which were reported some time ago (6), and for which structural information is available from X-ray crystallography (7, 8).

We now report the preparation of a small number of neutral adducts of the indium dihalides, which on the basis of the vibrational spectra are believed to contain indium–indium bonds. Again these are similar to the gallium analogues which were reported recently by Worrall *et al.* (9), although it appears that the symmetry and coordination number at the metal may not be the same for both sets of compounds.

[1]Permanent address: Department of Chemistry, University of Auckland, Auckland, New Zealand.

[2]To whom all correspondence should be addressed.

Experimental

General

Spectroscopic and analytical procedures were as described previously (1). Indium dihalides were prepared from indium metal and indium trihalides (3). N,N,N',N'-Tetramethylethylenediamine (TMED) and other ligands were the commercially available materials used without further purification. Solvents were refluxed in sodium/benzophenone and distilled from the blue ketyl. All operations were performed in an atmosphere of pure, dry nitrogen.

Preparative

The same general method was used in each case, with isolation procedures which varied according to the particular system. Approximately 2–3 mmol of the dihalide (calculated as the dimer) was placed in a Schlenk flask and 30–40 m of benzene syringed in through a rubber septum. The resultant suspension was frozen in liquid nitrogen, and a four-fold excess of monodentate, or two-fold excess of bidentate, ligand syringed in; solid ligands were dissolved in the minimum amount (5–10 mL) of benzene for this purpose. The liquid nitrogen cooling bath was removed, and the system stirred as soon as the melting of the solvent allowed. Magnetic stirring was continued for 20 min after the solvent had completely melted.

Isolation procedures

InBr₂/TMED: The white suspension was filtered and the solid collected and dried. Analysis established the composition $InBr_2(TMED)$ for this material. The mother liquors were allowed to stand over a period of 72 h, when large crystals (1.5 × 0.5 × 0.5 cm) were obtained, with further smaller (1 × 1 × 2 mm) crystals being obtained from the residual liquid after 24 h. These crystals had the composition $In_2Br_4(TMED)_2C_6H_6$ (see Table 1 for analytical results).

InI₂/TMED: A red colour, believed to indicate the presence of InI, was still apparent after stirring at room temperature for 2.5 h, and the mixture was therefore refluxed for 2 h. The yellow solid which separated on cooling was collected and dried, and found to have the composition $InI_2(TMED)$. The filtrate was concentrated to 20 mL and a viscous brown liquid settled out on standing. This oil was separated and treated with 10 mL of light

ligroin (40–60°C bp) to yield a sticky yellow solid which was exhaustively pumped at room temperature. Analysis showed the composition of this material to be $In_2I_4(TMED)_2C_6H_6$.

$InBr_2/Et_3P$: When these two substances reacted in toluene at −40°C, a deep red solution initially formed but this rapidly changed colour, becoming yellow at about −20°C, and at room temperature, appreciable decomposition to the metal was noted. Addition of cold light ligroin to the solution at −20°C produced a white precipitate which was collected and dried; analysis gave the empirical formula $InBr_2 \cdot Et_3P$. The instability of this material prevented further investigation; in particular the infrared and Raman spectra presented no identifiable features.

InI_2/Et_3P: The green reaction mixture was concentrated to 20 mL by evaporation; after 2–3 h the orange crystalline material which was deposited was collected and dried. Further material was obtained by addition of light ligroin to the solution. Analysis showed this solid material to be $InI_2 \cdot Et_3P$.

Other reactions

Reactions between benzene solutions of $InBr_2$ and the ligands Et_3N, pyridine, 2,2'-bipyridine, and dimethylsulphoxide all gave indium metal in yields of 90% or larger, according to the disproportionation reaction

$$3InX_2 \rightarrow In^0 + 2InX_3$$
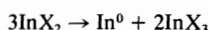
In the case of $InBr_2/Et_3P$, a substance of stoichiometry $InBr_3 \cdot 2Et_3P$ was recovered from the mother liquor, while $InBr_2 + Ph_3P$ yielded 100% InBr according to

$$In_2Br_4 \rightarrow InBr + InBr_3$$

Similar behaviour was observed with InI_2 and Et_3N, pyridine, 2,2'-bipyridine, Ph_3P, and bis(diphenylphosphino)ethane.

All attempts to make chloro-derivatives by the above methods from $InCl_2$ and a number of neutral donors resulted in disproportionation to indium metal.

Results and discussion

General

The presence of coordinated ligands is apparent from the analytical results, and from infrared spectroscopy. The ir spectrum of neat TMED has bands *inter alia* at 1040 and $1275 \, cm^{-1}$, which are shifted to 1025 and $1295 \, cm^{-1}$ in the complexes, suggesting that they are related to the vibrations of the donor atom (10). Similarly bands at 1230 and $975 \, cm^{-1}$ in the spectrum of Et_3P (11) shift to 1265 and $995 \, cm^{-1}$ in the complexes. ^{1}H-nmr spectra of the products in deuteroacetonitrile also confirmed the presence of the ligands, without adding to our knowledge of the structures of the complexes. The

TABLE 1. Analytical results[a]

Compound	% In	% halogen
$In_2Br_4(Et_3P)_2$	29.0(29.3)	41.0(40.7)
$In_2Br_4(TMED)_2$	32.7(29.4)[b]	39.2(40.9)[b]
$In_2Br_4(TMED)_2C_6H_6$	26.8(26.7)	37.3(37.2)
$In_2I_4(Et_3P)_2$	24.1(23.6)	52.1(52.2)
$In_2I_4(TMED)_2$	23.6(23.7)	52.9(52.4)
$In_2I_4(TMED)_2C_6H_6$	22.2(21.9)	48.4(48.5)

[a] Figures in parentheses indicate theoretical compositions.
[b] See text for discussion of these analyses.

magnetic susceptibilities of the solid materials (0.01–0.05 BM at 25°C) established them as diamagnetic. Rapid decomposition in suitable solvents prevented the measurement of molar conductivities.

Sharp aromatic resonances (7.20 ppm downfield from TMS) confirmed the presence of benzene in those products formulated as $In_2X_4(TMED)_2C_6H_6$. Neither nmr nor vibrational spectroscopy throws any light on the mode of interaction of benzene in the solid phase of such compounds, and only minor changes in other frequencies were noted on comparing analogous solvated and non-solvated compounds. This may indicate that the benzene is merely trapped in the crystal lattice with no strong interactions towards the metal centre, and in keeping with this, the crystalline materials slowly lose benzene and disintegrate on standing in an atmosphere of dry nitrogen, which frustrated attempts at X-ray structural analysis.

Vibrational spectroscopy

In view of the above results, we conclude that the most obvious structural analogues of these compounds are the $Ga_2Cl_4L_2$ compounds reported by Worrall *et al.* (9), and shown to involve Ga—Ga bonding. The presence of In—In bonds in the corresponding indium(II) anionic complexes also provides further indication of a metal–metal bonded structure, and in the absence of X-ray crystallographic data (see above) we now justify the formulation of the present compounds as In—In bonded dimers on the basis of vibrational spectroscopy.

As a preliminary, we first report some necessary revision to the previously published results for the $In_2X_6^{2-}$ anions. Despite the earlier report (5), we now find that these compounds dissolve in CH_3CN with only slight decomposition, and that addition of Et_2O yields good crystalline material. The vibrational spectra of these products are similar to those of the untreated materials, except that the highest frequency infrared features, at $332 \, cm^{-1}$ for Cl, $235 \, cm^{-1}$ for Br, and $186 \, cm^{-1}$ for I, have disappeared; an additional feature is also observed at $135 \, cm^{-1}$ for $In_2I_6^{2-}$. We suggest that such absorptions are actually due to tetrahaloindate(III) anion impurities (12). The simplified spectra of the $In_2X_6^{2-}$ anions are summarized in Table 2, from which it is clear that it is no longer necessary to invoke Fermi resonance in order to explain the spectra (cf. ref. 5). Other infrared frequencies, and the Raman spectra, which remain unchanged in the newly purified materials, are not affected. These

TABLE 2. The revised infrared spectra of $In_2X_6{}^{2-}$ anions, as Bu_4N^+ salts (in cm^{-1})

$In_2Cl_6{}^{2-}$	$In_2Br_6{}^{2-}$	$In_2I_6{}^{2-}$	Assignment	Description
292s	207s	162s	E_u	$v(In—X)$
284sh	185s	135s	A_{2u}	$v(In—X)$

revisions must have some effect on the values of the force constants and potential energy distributions, but do not change the general conclusions reached earlier about the $X_3In—InX_3{}^{2-}$ structure of these anions.

The Raman and ir features of $In_2X_4L_2$ ($X = Br, I$; $L = TMED, Et_3P$) are detailed in Table 3. The most prominent feature in the spectra of each of the In_2X_4 complexes is a strong Raman line which appears at $141\,cm^{-1}$ in $In_2Br_4(TMED)_2$, at $110\,cm^{-1}$ in $In_2I_4(TMED)_2$, at $116\,cm^{-1}$ in $In_2I_4(Et_3P)_2$. These values agree well with the frequencies for $v(In—In)$ in the corresponding anionic species $In_2X_6{}^{2-}$ (5), and the shift of this stretching mode with changes in net charge or coordination number follows the pattern already established for the analogous Ga_2X_4 species (9).

Triethylphosphine complexes

Once the presence of a metal-to-metal bond has been established, various ionic structures can be ruled out, but even then a number of different structural possibilities must be considered for the TMED complexes; we return to this point below. A structural formulation is most easily made in the case of $In_2I_4(Et_3P)_2$. The mutual exclusion rule identifies the species as centrosymmetric, and on this basis we propose a structure of C_{2h} skeletal symmetry shown in Fig. 1. The vibrational representation for the stretching modes of this $In_2X_4P_2$ kernel is $3A_g + B_g + A_u + 2B_u$, in which the g-modes are Raman-active and all u-modes infrared-active. It was not possible to obtain satisfactory spectra for $In_2Br_4(Et_3P)_2$ (see Experimental), but the vibrational spectrum of $In_2I_4(Et_3P)_2$, given in Table 3, shows the $v(In—In)$ vibration, together with bands which are reasonably attributed to the four In—I stretching modes.

The assignment of phosphorus-to-metal stretching frequencies has generally raised some difficulties. Shobatake and Nakamoto (13) used metal isotope techniques for $NiX_2(Et_3P)_2$ and thus located $v(Ni—P)$ near $270\,cm^{-1}$. The spectra of $InX_3(R_3P)_2$ ($X = Cl, Br, or I$; $R = Me$ or Et) did not reveal any obvious $v(In—P)$ modes (14), but a single-crystal study of $InCl_3(Me_3P)_2$ lead to the identification of the totally symmetric modes of this molecule, with

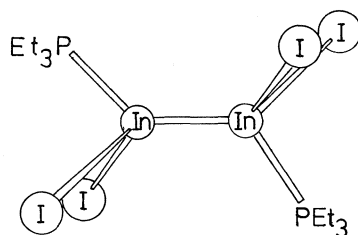$v(In—P)$ being assigned at $135\,cm^{-1}$ (15). This frequency seems rather low in terms of mass considerations, when compared to values of $307\,cm^{-1}$ for $v(In—Si)$ in $In(SiMe_3)_3$ (16), of $370–380\,cm^{-1}$ for $v(In—S)$ in a series of toluene-3,4-dithiol derivatives of indium (17), and of $319–339\,cm^{-1}$ for this mode in $InX_3·2Et_2S$ ($X = Cl, Br$) (18). The situation is undoubtedly complicated by the possibility of mixing modes of like symmetry. The present spectra contain bands at $376\,m$ (ir) and $333\,m\,cm^{-1}$ (R), shown elsewhere (13) to be $\delta(CCP)$ modes of the coordinated ligand. This leaves a weak ir band at $254\,cm^{-1}$, which we tentatively assign to $v(In—P)$.

N,N,N′,N′-Tetramethylethylenediamine complexes

In the TMED series, we first consider the In—halogen stretching region, where in all cases two Raman and two non-coincident ir features are found (Table 3). This suggests the presence of a centrosymmetric In_2X_4 unit, which requires the $In_2X_4N_4$ kernel to adopt a conformation similar to that in the Et_3P analog. Inspection of the In—N stretching region, as defined by Mertz *et al.* (19), might argue against the presence of a centre of symmetry since all four features are coincident, or nearly so, but in the context of the above discussion, we attribute this to a lowering of the overall molecular symmetry caused by the hydrocarbon framework of the ligand.

The frequencies of coordinated TMED have been reported previously (20), and we assume that the ligand is functioning as a bidentate donor in the present complexes, as implied by the presence of four $v(In—N)$ frequencies. This requires the indium atoms in $In_2X_4(TMED)_2$ to be five-coordinate, and the shift in the $v(In—In)$ frequency from $116\,cm^{-1}$ in $In_2I_4(Et_3P)_2$ to $110\,cm^{-1}$ in $In_2I_4(TMED)_2$ is consistent with an increase in coordination number from four to five. This conclusion, and the identification of a centrosymmetric In_2I_4 unit, reveal notable differences between these indium complexes and the gallium compounds $Ga_2Cl_4(dioxane)_2$, in which the dioxane is monodentate, the metal atoms are four-coordinate, and the molecular symmetry approximately C_{2v} (9). We note in this context that some examples of five-coordination at tin are known for Sn—Sn bonded compounds (21).

The mode of coordination of $N,N,N′,N′$-tetramethylethylenediamine requires some comment. As already noted, the expected bidentate coordination seems to be confirmed by the number of bands observed in the $350–500\,cm^{-1}$ region of the spec-

trum (v(In—N)). This still leaves at least three possibilities to consider: (*a*) terminal TMED, (*b*) intermolecular bridging, and (*c*) intramolecular bridging. The second possibility can be rejected in view of the results for the 700–900 cm^{-1} region of the infrared spectrum. Chelate-type diamines display two bands, assigned as CH_2 rocking vibrations at approximately 810 and 770 cm^{-1}, while intermolecular bridging leads to a *trans* conformation in the diamine, with ir bands at 870 and 790 cm^{-1} (10, 20). Our materials show bands at 770w and 790s, implying a *cis* or *gauche* conformation of bidentate TMED, and the structures are accordingly written as X_2(TMED)InIn(TMED)X_2.

Some spectral features still remain unexplained after this analysis. Several of these can be ascribed to small amounts of impurities, as is the case of In_2Br_4(TMED)$_2C_6H_6$ where a Raman line at 197 cm^{-1}, and an ir feature at 236 cm^{-1}, point to the presence of InBr$_4^-$. Perhaps more interesting is the strong Raman line found at 129 cm^{-1} in the spectrum of In_2Br_4(TMED)$_2$. The intensity and position of this feature suggest the presence of a second metal–metal bonded species, with the frequency of this vibration affected either by a higher coordination number, or by an increase of negative charge, or both. As can be seen from Table 1, the analyses for this material do not agree particularly well with the presumed composition, so that the presence of some unidentified second compound in the crude material is not unreasonable. Our interpretation has also neglected the presence of bending modes, which will be responsible for some of the features still unexplained in the assignments in Table 3.

Reaction pathway

Although the reaction is apparently the single addition of neutral ligand to indium dihalide, two significant factors must be recognized. The first is that few of the InX$_2^-$ ligand combinations investigated do in fact yield the desired product, and that in most cases disproportionation to In^0 and presumably In^{III} species predominates. The second is that a deep-red or orange colour is formed on the

TABLE 3. Vibrational spectra of $In_2X_4L_2$ (in cm^{-1})

In_2Br_4(TMED)$_2$		In_2Br_4(TMED)$_2C_6H_6$		In_2I_4(TMED)$_2$		In_2I_4(TMED)$_2C_6H_6$[b]	In_2I_4(Et$_3$P)$_2$		Assignment[a]
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Infrared	Raman	
488m	490m	487m	492m	480m		486ms			v(In—N)
460w, br	461w	462w	468w	458w		466w			
440m	441vw	442m	445vw	436m		443ms			
397vw	397w	398vw	385vw, br	378w		380w			
362vw	368vw	367vw		362vw		354w			
							254vw		Unassigned
									v(In—P)?
	233vw		240m	220m	211w	200m, br		202w	Unassigned
210s	188w	210s	175w	160m	137m	172m	178vs	169w	v(In—X), $A_g + B_g + A_u + B_u$
190s, br	141s	192s, br	139s	144m	110s	148s	152vs	116s	v(In—In), A_g
152s, br	155sh	153m, br				106s			Bending modes
128m	129s	128m		130sh		95sh			
103m	86m	102m	86m						

[a]All species were assigned on the basis of C_{2h} symmetry for the In_2X_4 kernel.
[b]Raman data not available.

addition of either anionic (5) or neutral ligands (this work) to solutions of indium dihalide, which is compatible with the establishment of the equilibrium

$$In_2X_4 \rightleftharpoons InX + InX_3.$$

Since very little is known about the solution chemistry of indium(I) or indium(II) compounds in aromatic solvents, we are presently unable to rationalize these various observations, and work on these and related problems is continuing.

Acknowledgement

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