Co-ordination Compounds of Indium. Part XXXI.[1] Further Studies of Anionic Complexes of Indium(I)

By **Jacob J. Habeeb** and **Dennis G. Tuck**,* Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada

The reaction of cyclopentadienylindium(I) with equimolar quantities of HX and $[NEt_4]X$ in organic media yields crystalline $[NEt_4][InX_2]$ (X = Cl, Br, or I). Vibrational spectroscopy shows that these new indium(I) species are bent monomeric anions (*cf.* SnX_2). A new salt of the previously identified anion $[InI_3]^{2-}$ has also been obtained by this route. Salts of $[InI_2]^-$ and $[InI_3]^{2-}$ can also be prepared electrochemically. Metathetical reactions give rise to $[In(NCO)_2]^-$, $[In(NCS)_2]^-$, and $[In(NCS)_3]^{2-}$; bridging by the ligands may be an important feature of the structure of salts of these anions.

THE extension of the knowledge of the chemistry of the lower oxidation states of indium has been the aim of recent work in this laboratory; a recent review[2] has emphasised the scant information available on the complexes of In^I. We have previously reported[3] the preparation of crystalline anionic halide compounds of In^I by the simple reaction (1) in methanol (X = Cl, Br,

$$[Me_2bipy]X_2 + InX(s) \longrightarrow [Me_2bipy][InX_3] \quad (1)$$

or I; $[Me_2bipy]^{2+}$ = *NN'*-dimethyl-4,4'-bipyridinium dication). The vibrational spectra[4] of these compounds are in agreement with the pyramidal structure to be expected of species which are isoelectronic with the $[SnX_3]^-$ anions, conclusions which have been supported by force-constant calculations.[5] The main disadvantage in the procedure (1) lies in the properties of the cation, which is a redox indicator[6] and which gives rise to an undesirably profuse vibrational spectrum, which is a major problem in the study of the anions and their derivatives. Attempts to replace this cation with other dipositive organic cations, notably derivatives of 1,2-bis(diphenylphosphino)ethane, were unsuccessful. We now report the preparation of salts of $[InX_3]^{2-}$ by an alternative route, and the preparation and study of some $[InX_2]^-$ anions (X = Cl, Br, I, CNS, or CNO). A preliminary account of part of this work has already been published.[7]

RESULTS AND DISCUSSION

Preparations involving Cyclopentadienylindium(I).—The compound cyclopentadienylindium(I), In(cp),[8] is one of two organoindium(I) compounds known, the

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other being the methylcyclopentadienyl derivative.[9] A recent study [10] demonstrated the usefulness of In(cp) as a starting material for the synthesis of neutral indium(I) compounds, and we have now extended this work to anionic species. In an experiment designed to parallel the earlier work,[3,6] In(cp) in benzene was mixed with an ethanolic solution of 1,2-bis(methyldiphenylphosphonio)-ethane iodide, $[Me_2dppe]I_2$, also containing an equimolar quantity of HI; a white precipitate of the corresponding salt of $[InI_3]^{2-}$ formed when the solution was cooled [*cf.* equation (2)]. This compound is exactly analogous to the $[InI_3]^{2-}$ salt studied earlier. (Analytical results for this and other compounds are given in Table 1.)

Table 1

Analytical results (%) for indium(I) compounds

Compound	Found		Calc.	
	In	Halogen or pseudohalogen	In	Halogen
(*a*) Preparation *via* In(cp)				
$[NEt_4][InCl_2]$ [a]	36.4	21.9	36.5	22.2
$[NEt_4][InBr_2]$	28.2	39.1	28.4	39.5
$[NEt_4][InI_2]$	23.3	51.1	23.1	50.9
$[NEt_4][In(NCS)_2]$	31.3	31.8	31.9	32.1
$[NEt_4][In(NCO)_2]$	34.7		35.0	
$[Me_2dppe][InI_3]$ [b]	12.8	40.9	12.4	41.2
$[Me_2dppe][In(NCS)_3]$	16.3	24.4	16.2	24.3
(*b*) Electrochemical preparations				
InI	47.2	52.5	47.5	52.5
$[NEt_4][InI_2]$	23.0	51.1	23.1	50.9
$[Me_2dppe][InI_3]$ [b]	12.8	41.4	12.4	41.2

[a] Found: C, 29.8; H, 6.0; N, 4.4. Calc.: C, 30.5; H, 6.3; N, 4.5%. [b] $Me_2dppe^{2+} = [Ph_2MePC_2H_4PMePh_2]^{2+}$.

Previous work using this and other dipositive phosphonium cations in reactions with indium(I) chloride, bromide, or iodide suspended in various organic solvents [*i.e.* using procedure (1)] did not produce $[InX_3]^{2-}$ salts, the indium monohalide being recovered unchanged in each case.[11] We suggest that this may be because the phosphonium salts exist in solution as tightly bound ion triplets, so that the halide anion cannot readily react at the surface of the InX solid.

Reactions were also carried out between In(cp) and tetra-alkylammonium halides in the presence of the appropriate HX. In each case, the product was the compound $[NEt_4][InX_2]$ (X = Cl, Br, or I) irrespective of the In(cp) : $[NEt_4]X$ ratio in the reaction mixture (up to ratios of 1 : 3), so that the reaction stoicheiometry is as in (2). As in the case of the phosphonium cation

$$[NEt_4]X + HX + In(cp) \longrightarrow [NEt_4][InX_2] + Hcp \qquad (2)$$

discussed above, the preparation *via* In(cp) gives a compound which could not be obtained by another route; we have previously reported [4] the failure of InCl to dissolve in molten $[NEt_4]Cl$, a reaction designed to produce $[NEt_4][InCl_2]$ or $[NEt_4]_2[InCl_3]$. The bromo- and iodo-compounds can also be obtained from $[NEt_4][InCl_2]$ by reaction with either sodium bromide or iodide in hot ethanol–benzene, from which NaCl precipitates. Similar metathetical reactions yield the corresponding cyanate and isothiocyanate compounds (see below).

Electrochemical Preparation.—The anodic oxidation and dissolution of metals in aqueous media is a well known procedure, but the application of this method to non-aqueous systems appears to have been given little or no attention. We have now shown that a variety of main-group and transition metals can be oxidised electrochemically in the presence of suitable reagents to yield co-ordination compounds. The unusual feature of these procedures is that the solution phase is an organic solvent, which in the case of the present work was ethanol–benzene (1 : 1). A platinum cathode was used throughout, while the anode was a piece of indium metal hammered on to a platinum-wire support.

When a voltage of 50—100 V was applied across a cell containing iodine and a trace of $[NEt_4]I$, a purple layer of indium(I) iodide formed on the anode surface. This material eventually deposited on the floor of the cell and could be collected. With approximately equimolar quantities of iodine and $[NEt_4]I$, the product deposited is white crystalline $[NEt_4][InI_2]$; the progress of the reaction can be judged both by the discharge of the iodine colour of the solution, and the disappearance of the indium metal. The compound $[Me_2dppe][InI_3]$ was obtained in an analogous reaction. This method cannot be used to prepare indium(I) derivatives of chloride or bromide, since in these circumstances the products are the corresponding indium(III) compounds.[12]

The mechanism of this process is far from clear at the present time, since the nature of the solution phase is such that the normal concepts of electrochemistry are not readily applicable, but the usefulness of the method seems beyond question. The current efficiency is low (<10%) [11] and the high applied voltage may simply be producing surface-charging effects, which could be crucial to the oxidation process, rather than setting up the normal Faraday electrolysis. Experiments aimed at elucidating the mechanism of the anodic oxidation are under way. We have also successfully applied this

Table 2

Vibrational spectra (cm^{-1}) of $[InX_2]^-$ anions in crystalline $[NEt_4][InX_2]$ (X = Cl, Br, or I), and of SnX_2 (X = Cl or Br) in solid argon or nitrogen matrices

Ion	Raman	I.r.			Raman		I.r.
					Ar	N_2	
$[InCl_2]^-$	328	330m	$SnCl_2$	ν_1	341	353	354
	177			ν_2	124		
	291	291m		ν_3	320	322	334
$[InBr_2]^-$	236	235	$SnBr_2$	ν_1	244	237	
				ν_2	82	84	
	197			ν_3	231	223	
$[InI_2]^-$	186						
	140						

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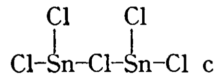
technique to the preparation of cationic, neutral, and anionic compounds of a variety of transition and main-group elements.[12]

Vibrational Spectroscopy of $[InX_2]^-$ *Anions.*—The vibrational spectra of the $[InX_2]^-$ anions over the range 200—400 (i.r.) and 100—400 cm^{-1} (Raman) are shown in Table 2, as are the corresponding data for the iso-electronic tin(II) species. The halides of Sn^{II} are known to exist as bent monomeric species in the gas phase.[13] In the solid state, $SnCl_2$ is described as a layer structure of  $\text{Cl–}\overset{\overset{\text{Cl}}{|}}{\text{Sn}}\text{–Cl–}\overset{\overset{\text{Cl}}{|}}{\text{Sn}}\text{–Cl}$ chains,[14-16] and SnI_2 has a similar structure.[17] The vibrational spectra of $SnCl_2$ and $SnBr_2$ have been recorded in the gas phase,[18,19] and in low-temperature matrices of argon and nitrogen.[20,21] These latter are the results quoted in Table 2.

The spectrum of $[InCl_2]^-$ is in good agreement with that of monomeric $SnCl_2$, and we therefore assign the bands as shown in Table 2 on the basis of a bent $[Cl{-}In{-}Cl]^-$ unit. In general, the values in Table 2 confirm the formulation of the compounds prepared as $[NEt_4][InX_2]$ salts. The instability of these substances in nitromethane and similar solvents prevented any conductimetric investigation.

Indium*(I) *Pseudohalide Compounds.—A number of anionic and neutral pseudohalide derivatives of In^{III} have been reported previously (see ref. 2 for a review of this topic). Spectroscopic evidence shows that in this oxidation state, indium (like other Group 3 elements) [22] has A-type behaviour, in that the thiocyanate ligand bonds to the metal *via* the nitrogen atom. It was therefore of interest to prepare and study the corresponding indium(I) species, in the hope of identifying the mode of ligation. Tetraethylammonium dichloroindate(I) reacts with 2 mol of sodium cyanate in ethanol, precipitating sodium chloride quantitatively, to yield $[NEt_4][In(NCO)_2]$. Analogous reactions gave $[NEt_4][In(NCS)_2]$ and $[Me_2dppe][In(NCS)_3]$.

The question of the identification of the mode of bonding of ambidentate pseudohalide ligands from vibrational spectroscopy has been discussed in detail by Norbury,[23] and by Bailey *et al.*[24] Perhaps the one reliable fact is that, despite earlier pronouncements, there is no diagnostic criterion which can distinguish unambiguously between *N*- and *S*-bonded thiocyanate on the basis of vibrational spectra. For the anion $[In(CNS)_2]^-$, using CNS for the moment without prejudice, $\nu(C{\equiv}N)$ is at 2 077vs cm^{-1}, with a band at 486m cm^{-1}, assigned to δ(NCS). These two vibrations point to *N*-bonding, in which case $\nu(C{=}S)$ would be expected at *ca.* 800 cm^{-1}. This region is obscured by a strong cation band at 790 cm^{-1}, but we did observe an absorption at 694m cm^{-1}, a wavenumber normally associated with $\nu(C{=}S)$ of *S*-bonded thiocyanate. Vibrations at 265m and 247 (sh) cm^{-1} are in the region for ν(In–N), but not enough is known about such frequencies to rely on this assignment. A possible explanation of these observations is that in the solid state the anions are in a polymeric form similar to that of solid $SnCl_2$, with both bridging and *N*-bonded unidentate thiocyanate ligands. Chamberlain and Moser [25] have studied the i.r. spectrum of $Sn[NCS]_2$, and conclude that extensive bridging occurs in this structure, and to a lesser extent in salts of the $[Sn(NCS)_3]^-$ ion. The spectrum of the salt $[Me_2dppe][In(NCS)_3]$ is very similar to that of the $[In(NCS)_2]^-$ compound, namely ν(CN) at 2 077vs, ν(CS) at 690m, and δ(NCS) at 486m cm^{-1}; no bands were detected in the metal–ligand stretching region. Our conclusions therefore again emphasise the structural similarities between indium(I) and tin(II) species.

The i.r. spectrum of $[NEt_4][In(NCO)_2]$ has ν(CN) at 2 175 and 2 195s cm^{-1}, slightly lower wavenumbers than those reported for the neutral adducts of indium(III) cyanate.[26] Other anion vibrations are at 1 262m [$\nu(C{=}O)$] and 280m and 250(sh) cm^{-1} [ν(In–ligand)]; the δ(NCO) region is partially obscured by cation bands. Again, the results do not distinguish between *N*- or *O*-bonded cyanate, and both bridging and terminal ligands may be present in the solid.

In general, the present studies of anionic indium(II) pseudohalide complexes do not reveal any striking change from A to B character between In^{I} and In^{III}. In particular, both oxidation states form anionic isothiocyanato-compounds,[27] and while $[In^{I}(NCS)_2]^-$ apparently involves NCS bridging of metal ions, this behaviour is also observed in the neutral indium(III) compound.[28] Any distinction between the relative hardness of In^{I} and In^{III} must therefore await a more sensitive probe than that used in the present work.

EXPERIMENTAL

General.—Analytical and spectroscopic methods were as described in earlier papers.[19,27,28] No satisfactory method has been found for cyanate analysis (*cf.* ref. 26) and we therefore rely on metal analysis, and the experimentally determined stoicheiometry of the metathetical preparation. Solvents used in reactions involving In(cp) were carefully dried before use. All reactions were under nitrogen.

Preparations via *In(cp).*—A solution of hydrogen halide (HX) in ethanol (10 cm^3) was prepared, the HX concen-

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tration determined titrimetrically, and an equimolar quantity of $[NEt_4]X$ (*ca.* 2 mmol) added. This solution was added dropwise to an equimolar quantity of In(cp) in dry benzene (50 cm^3). The resulting mixture was cooled (0 °C) for *ca.* 1 h, when colourless crystals of tetraethylammonium dihalogenoindate(I) were produced. These were washed with benzene and diethyl ether, and dried *in vacuo* at 25 °C. Yields were usually $>75\%$.

The salt $[Me_2dppe]I_2$ was obtained by methylating $Ph_2PC_2H_4PPh_2$ with methyl iodide. The preparation of $[Me_2dppe][InI_3]$ then followed the route described above.

Metathetical Reactions.—As an alternative to the preparation *via* In(cp), we found that the $[InBr_2]^-$ and $[InI_2]^-$ salts could be obtained by mixing hot (*ca.* 70 °C) ethanol solutions of $[NEt_4][InCl_2]$ and NaBr or NaI. The white precipitate which formed when the mixture was cooled to 10 °C was shown to be NaCl, free of Br^- or I^-, and the composition of the products obtained by removing solvent from the filtrate was confirmed by indium and halogen analysis.

A similar procedure involving $[NEt_4][InCl_2]$ and sodium thiocyanate yielded $[NEt_4][In(NCS)_2]$. For the preparation of the cyanate, the weight of precipitated NaCl (62.0 mg) was in good agreement with that expected for complete substitution (63.3 mg). This result, and the indium analysis, served to characterise $[NEt_4][In(NCO)_2]$ in the absence of a suitable method for cyanate determination (*cf.* ref. 26).

Electrochemical Preparation of $[NEt_4][InI_2]$.—Indium metal (*ca.* 0.5 g; say 4 mmol) hammered on to a platinum wire formed a plate-like anode, and a second platinum wire was the cathode of the cell. The solution phase consisted of *ca.* 100 cm^3 of ethanol–benzene (1 : 1) containing iodine (8 mmol) and tetraethylammonium iodide (4 mmol). The temperature was maintained at *ca.* 20 °C throughout. The applied voltage was >50 V, and the current 30 mA. After 3 h, the colour of the iodine was completely discharged, and crystals of $[NEt_4][InI_2]$ were recovered from the bottom of the cell. The conditions for the preparation of $[Me_2dppe][InI_3]$ were essentially identical.

In a subsequent experiment, only trace amounts of $[NEt_4]I$ were used, but again with *ca.* 8 mmol of iodine. The formation of purple InI on the anode was quickly apparent; after electrolysis for 2 h, InI (*ca.* 0·75 g) was recovered from the bottom of the cell.

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