Co-ordination Compounds of Indium. Part XXV.[1] Dihalogeno(acetylacetonato)indium(III) Complexes

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The indium(I) halides react with refluxing acetylacetone (Hacac) to give a mixture of In(acac)$_3$ and InX$_2$(acac). The latter compound could not be isolated in a pure form, but reactions with nitrogen donors give the crystalline solids [InX$_2$(acac)L^{II}]EtOH (L^{II} = 2,2'-bipyridyl or 1,10-phenanthroline) and [InX$_2$(acac)L$_2$]EtOH (L = pyridine or [^{2}H$_5$]pyridine). The spectral properties confirm the formulation of this group of compounds as six-co-ordinate indium(III) complexes with an InX$_2$O$_2$N$_2$ kernel.

THE ligand acetylacetonate (pentane-2,4-dionate anion, acac) is known to form a series of chelate complexes with metal ions, and a good deal of attention has been given to those compounds in which the number of ligands is equal to the oxidation state of the metal. Indium(III) is no exception to this. Tris(acetylacetonato)indium(III) was first reported by Morgan and Drew [2] in 1921, and more recently a related series of compounds involving trifluoromethyl-β-diketonates has also been prepared.[3] In addition, the compound Me$_2$In(acac) has been obtained *via* the reaction of trimethylindium and acetylacetone.[4]

We now report the formation of compounds of the type [InX$_2$(acac)L$_2$], where X = Cl, Br, or I, and L = pyridine, and [InX$_2$(acac)L^{II}], where L^{II} = 2,2'-bipyridyl or 1,10-phenanthroline. One of the interesting features of this work has been the unusual preparative route, which involves the reaction of indium(I) halides with an excess of acetylacetone. The brown solid which is

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[1] Part XXIV, J. G. Contreras and D. G. Tuck, *J. Organometallic Chem.*, 1974, **66**, 405.

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[4] H. C. Clark and A. L. Pickard, *J. Organometallic Chem.*, 1967, **8**, 427.

initially formed reacts with neutral donors to give crystalline solids. The indium(I) halides are insoluble and generally unreactive compounds, and this new reaction with acetylacetone suggests a number of possible applications of this method in the preparation of complexes of indium(III), and other metal ions.

EXPERIMENTAL

General and Spectroscopy.—I.r. spectra were obtained with Beckman IR12 (500—200 cm^{-1}) and Perkin-Elmer 457 (4000—500 cm^{-1}) spectrophotometers and Raman spectra on a Cary 81 instrument. Mass spectra were obtained with a Hitachi–Perkin-Elmer RMU6E spectrometer. A Radiometer CDM2d instrument was used in conductivity measurements, which were carried out in acetonitrile. In the case of the complexes with [$^2H_5$]pyridine, a few drops of anhydrous methanol were required to dissolve the compounds, and conductivities obtained in this way were corrected for the conductivity of the solvent. M.p.s given are uncorrected; in many cases, the compounds melted with decomposition.

TABLE 1

M.p.s, conductivity, and analytical results for [InX_2(acac)L^{II}]EtOH and [InX_2(acac)L_2]EtOH compounds

				Found (%)					Required (%)				
	X	M.p. (t/°C)	Molar [a] conductivity	C	H	N	In	X	C	H	N	In	X
L^{II} = bipy	Cl	252 [b]	1·56	41·9	4·0	5·3	23·5	14·7	41·3	4·3	5·8	23·6	14·6
	Br	248 [b]	1·46	35·0	3·1	5·0	19·9	27·7	35·4	3·6	4·9	19·9	27·8
	I	218 [b]	1·01	30·9	2·8	4·0	17·1	37·8	30·5	3·1	4·2	17·1	37·9
L^{II} = phen	Cl	293 [b]	1·70	44·3	3·5	5·8	22·6	13·7	44·6	4·1	5·5	22·5	13·9
	Br	*c*	1·00	38·2	3·1	4·8	19·4	26·7	38·0	3·5	4·7	19·1	26·6
	I	*c*	1·80	32·8	2·9	4·0	16·5	36·5	32·9	3·0	4·0	16·5	36·6
L = py	Cl	244 [b]	1·00	41·3	4·9	5·8	23·4	14·6	41·8	4·7	5·7	23·5	14·5
	Br	234 [b]	1·70	35·6	3·5	4·9	20·0	27·8	35·3	3·9	4·8	19·9	27·7
	I	186 [b]	2·11	30·3	3·0	4·4	17·1	37·9	30·4	3·4	4·2	17·1	37·8
L = [$^2H_5$]py	Cl	248 [b]	1·08	40·6	3·9	5·9	23·0	14·2	40·9	3·6	5·6	23·0	14·2
	Br	239 [b]	1·03	34·8	3·4	4·7	19·7	27·3	34·7	3·1	4·8	19·5	27·2
	I	191	1·23	29·3	3·8	4·2	16·9	37·4	29·9	2·7	4·1	16·8	37·2

[a] Ω^{-1} cm^2; 10^{-3}M soln. in acetonitrile. [b] Melts with decomposition. [c] Decomposes prior to melting.

Preparative.—Indium(I) halides were obtained by procedures described previously.[5] Acetylacetone (Fisher Scientific) was used as supplied.

The complexes were prepared by a standard method. A quantity (1—2 mmol) of the appropriate indium(I) halide was refluxed for 24 h with an excess of acetylacetone (*ca.* 10 ml) under nitrogen. At the end of this period, a brown solid was visible in the reaction vessel. ^1H N.m.r. investigation of this pasty substance suggested that it was a mixture of $In(acac)_3$ and polymeric InX_2(acac), but we were unable to separate and characterise a pure sample of the latter compound. After removal of the excess of acetylacetone, the brown solid was dissolved in anhydrous ethanol, and the appropriate ligand added, dissolved in ether (bipyridyl), dichloromethane (phenanthroline), or neat (pyridine and [$^2H_5$]pyridine). After a few minutes stirring, a pale yellow crystalline solid precipitated; this was filtered off, washed with dry ether, and dried *in vacuo*. The compounds so obtained are air-stable over a reasonable period of time.

Table 1 lists the analytical, m.p., and conductivity results for the compounds obtained. In every case, analysis showed that the compound contained one molecule of ethanol in addition to the [InX_2(acac)L] species. This ethanol could not be removed by heating, either in air or *in vacuo*. The compounds are all non-electrolytes in acetonitrile.

The brown solid obtained from the initial reaction dissolved in chloroform to give a brown solution. No immediate reaction was detected when pyridine, 2,2′-bipyridyl, or 1,10-phenanthroline was added to this solution; removal of the solvent after 3 h yielded a mixture of unreacted material. No products could be obtained by reaction of the brown solid with dimethyl sulphoxide, triphenylphosphine, bis(diphenylphosphino)ethane, or halide anion (in the form of tetra-alkylammonium halide) in ethanol.

RESULTS AND DISCUSSION

The Initial Reaction.—As noted in the introduction, the indium(I) halides are not noted for their reactivity. A small number of addition compounds[6,7] of undetermined structure have been reported, and oxidative insertion reactions into C—X (X = Br,[8] or I[9]), metal-metal,[10,11] I—I,[1] and S—S[12] bonds are known. The overall reactions between InX and Hacac obviously involve oxidation of the element, since the final products are neutral indium(III) species. The nature of the intermediate processes is suggested by the observations that indium metal was precipitated in the reaction involving indium(I) chloride (but not in the case of bromide or iodide), and that this metal redissolved after about one hour of refluxing. The tentative reaction scheme is:

$$\mathrm{InX} + \mathrm{Hacac} \longrightarrow \mathrm{H[In(acac)X]} \qquad (1)$$

$$\mathrm{H[In(acac)X]} + \mathrm{InX} \longrightarrow \mathrm{InX_2(acac)} + \mathrm{In^0} + 1/2\mathrm{H_2} \qquad (2)$$

$$\mathrm{In^0} + 3\mathrm{Hacac} \longrightarrow \mathrm{In(acac)_3} + 3/2\mathrm{H_2} \qquad (3)$$

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The postulated H[In(acac)X] species in (1) may in fact exist only as a solvated ion-pair, but the presence of two different indium(I) species seems necessary in order to account for the disproportionation to indium metal. The evolution of hydrogen was not observed directly, since the preparation involved refluxing under nitrogen. Although indium metal does not react under normal conditions, we have shown previously that freshly prepared metal surfaces react with weak acids (specifically acetic and formic acids,[13] which do not attack indium metal under normal conditions).

The presence of InX_2(acac) in the reaction mixture was confirmed by extracting the brown pasty solid with chloroform, when a white hygroscopic solid residue remained. This was identified analytically as $InCl_2$(acac),-$2H_2O$ (Found: C, 18·7; H, 3·3; Cl, 22·2; In, 35·6. $C_5H_9Cl_2InO_3$ requires C, 18·7; H, 3·4; Cl, 22·1; In, 35·8%). The n.m.r. spectrum of this compound in D_2O showed resonances at τ 4·37 and 7·97; for $In(acac)_3$ in $CDCl_3$, signals at τ 4·50 and 8·00 have been assigned to the γ-CH and methyl protons respectively.[14] It seems probable that $InCl_2$(acac) is highly hygroscopic, and that this species picks up moisture from solvents, *etc.*, to give the more stable $InCl_2$(acac),$2H_2O$.

The compounds reported are believed to be the first examples of six-co-ordinate indium in an $InN_2O_2X_2$ kernel. A related co-ordination is that in the $[InCl_2(bipy)_2]^+$ cations prepared by Walton.[15] It is unfortunate that the parent InX_2(acac) species could not be isolated, since no comparable solid compounds have been reported, although $GaBr_2$(tta) [tta = 1,1,1-trifluoro-4-(2′-thienyl)butane-2,4-dione] has been identified as a solution species in solvent extraction work.[16]

The presence of ethanol in all the adducts, deduced from the analytical results, was confirmed by i.r. absorptions at 3356s, 2985s, 1098ms, 880m, and 802ms cm^{-1}, and by strong peaks in the mass spectra corresponding to $C_2H_5O^+$. The failure to remove the ethanol molecule from these compounds under forcing conditions (including heating *in vacuo*) is surprising. It seems clear that the ethanol is not bonded to the indium, and that it is held more strongly than 'ethanol of crystallisation'; further work on this point is planned.

Mass Spectra.—The mass spectra of heated samples of solid were recorded for all the compounds prepared; temperatures were *ca.* 200° for bipy complexes, 260° for phen, and 100—150° for the pyridine compounds. In no case was a molecular ion peak observed.

The main feature of the mass spectra of these compounds is that the strongest peak is due to the nitrogen-donor ligand. All the spectra show a peak at *m/e* 45, assigned to $C_2H_5O^+$ ions, and another at *m/e* 115, due to In^+. No peaks due to the InL^+ species were detected, but peaks from $In(acac)^+$ and $In(acac)X^+$ were found in all cases, although the intensities were rather low. In the bipyridyl and phenanthroline complexes, peaks due to $In(acac)_2^+$ were detected. The $acac^+$ ion peak at *m/e* 100 was of very low intensity (*ca.* 10% of the nitrogen donor), emphasising that the acetylacetone is bonded much more strongly to the indium than is bipy, in keeping with the negative charge of the former.

For the pyridine complex $[InCl_2(acac)(py)_2]$EtOH, the mass spectrum was obtained over a range of temperatures from 70 to 160 °C. No significant changes in intensity, *etc.*, were observed with change in temperature, and the peak due to py^+ ions (*m/e* 79) was the most intense throughout, suggesting that the scission of the nitrogen-donor ligand is not due to thermal decomposition.

Vibrational Spectra.—The vibrational spectra of all twelve compounds prepared were recorded in both i.r. and Raman modes. We were able to confirm immediately that 2,2′-bipyridyl and 1,10-phenanthroline are indeed co-ordinated in these complexes, using the i.r. criteria proposed by a number of earlier authors.[17-19] The spectra of these two ligands seem to call for no further comment.

The assignment of indium–ligand vibrations was aided considerably by the use of $[^2H_5]$pyridine, and by comparing the spectra of related sets of compounds. Table 2 summarises our tentative assignments for the In—X, In—O, and In—N stretching modes. Most of these vibrations were observed as coincident i.r. and Raman bands, and the frequencies in the Table are averaged values; because of this, intensities are not given. There must be some reservation about the correct descriptions of these vibrations, since (for example) the bands assigned as ν(In—Br), ν(In—O), and ν(In—N) in $[InBr_2(acac)(py)_2]$EtOH are very similar in energy. There are a number of detailed comments to be made. In the $[InCl_2(acac)(bipy)]$ species, only one ν(In—N) band is observed, because the ν(In—Cl) modes at 306 and 285 cm^{-1} are both broad bands. The agreement between the bipyridyl and phenanthroline spectra is good, apart from the ν(In—N) vibrations. The In—Cl stretching frequencies are higher in the pyridine complexes than in the bidentate donor compounds; the reverse is true for the In—Br and In—I modes, which may imply a difference in stereochemistry between chloride and bromide (or iodide) compounds. The values are in general agreement with those reported for ν(In—X) in adducts of indium(III) halides.[20]

The symmetry of the InX_2O_2N kernel in these molecules cannot be higher than C_{2v} if the halogens are *trans*, and will be C_1 for *cis*-stereochemistry. The number of i.r. and Raman coincidences observed was extremely high, but although some bands were detected in one excitation

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mode only, we do not believe that the spectra permit a decision to be made as to the molecular symmetry.

The ν(In—O) frequencies are lower than the values previously assigned to this mode.[20] Hester and Plane [21] assigned a band at 444 cm^{-1} in In(acac) to ν(In—O), but while the vibration at this frequency may involve stretching of the In—O bonds, the energy appears too high for pure ν(In—O), in comparison with the relatively large number of ν(In—N) frequencies now reported in the 250—300 cm^{-1} region. We observed bands at 415 ± 3 and 430 ± 4 cm^{-1} in all the compounds prepared, in both Raman and i.r. spectra, but bands of *ca.* 420 cm^{-1} frequency have been reported for a number of acac complexes,[22] so that these can hardly be ν(In—O) vibrations.

TABLE 2

Low frequency vibrations in InX_2(acac) derivatives (in cm^{-1})

Halide / Donor	Cl			Br			I		
	ν(In—Cl)	ν(In—O)	ν(In—N)	ν(In—Br)	ν(In—O)	ν(In—N)	ν(In—I)	ν(In—O)	ν(In—N)
bipy	306	243	258	216	239	256	173	236	259
	284	205		182	203		141	205	
phen	302	?	295	209	243	293	164	247	297
	284		282	187		279	141		271
$(py)_2$	328	214	272	235	219	267	152	214	274
	290	189	256		188	246	132	188	256
$([^2H_5]py)_2$	334	213	275	246	220	274	157	214	279
	290	188	268		188	267	133	198	264

Supplementary Publication No. SUP 20983 (2 pp.) * lists the bands detected in the 400—1000 cm^{-1} region for the pyridine and [$^2H_5$]pyridine complexes, other than those noted above at 415 and 430 cm^{-1}. The assignment of the pyridine vibrations follows the work of Gill *et al.*,[23] and uses the notation of Kline and Turkevich.[24] In general, these spectra, and those discussed above, support the description of these compounds as six-co-ordinate $InX_2(acac)L_2$,EtOH complexes of indium(III).

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