

COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME 26

ANNÉE 1980

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**Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie**

Communications de la Faculté des Sciences de l'Université d'Ankara

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Complex Compounds of Indium (III) Chloride And Bromide With Some Organic Ligands.

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(Received January 10, 1980 and accepted March 6, 1980)

ABSTRACT

This work describes the preparations and properties of some new complexes of Indium (III). The ligands contain atoms from groups V and VI.

Indium (III) exhibits class "A" acceptor behaviour in which the strength of coordination is: $N > P$ and $O > S$.

Complexes of In (III) chloride and-bromide with organic ligands containing nitrogen or oxygen atoms as their potential sites of donation have been prepared.

The infrared of the formed complexes are discussed and an attempt to explain the type of coordinate bond is made. No evidence has been obtained for the formation of complexes with Me_2S , Me_2SO_2 , Ph_2S , Ph_2SO_2 , Ph_3P or Ph_3PS . This is probably because of the low donor strengths of sulphur and phosphorus atoms with respect to indium (III). Thermal stabilities of the adducts, molecular weights and the conductance of their solutions in organic solvents are measured.

The coordination chemistry of indium trihalides⁽¹⁾, perchlorate⁽²⁾, nitrate⁽³⁾ and lower halides⁽⁴⁾ have been investigated. Indium (III), like the corresponding boron, aluminium, and gallium compounds, readily forms addition compounds with a variety of donor molecules.

The purpose of the present work is to study systematically the reactions of indium trichloride and-bromide with organic

ligands containing atoms from Groups V and VI. In order to gain some information about the structure, mode of bond in the complexes and their thermal stabilities, the solid species have been prepared and examined.

From the present studies, it is concluded- that indium (III) exhibits class "A" acceptor behaviour in which the strength of the coordination is $N > P$ and $O > S$.⁽⁵⁾

Experimental

Infrared spectra were recorded on a Unicam SP 200G infrared spectrophotometer. Conductivities were measured using a Backman Electronic switchgear bridge model RA-2A with balance indicator. Molecular weights were measured using a vapour pressure osmometer model "Knauer". Thermogravimetric analysis was attempted using a Stato thermogravimetric balance. Considerable care was taken with the drying of solvents. Ethanol was boiled under reflux with magnesium ethoxide and then distilled. Other solvents were dried by conventional methods. Analyses of carbon hydrogen, and nitrogen were carried out by the microanalytical laboratory of El-Nasr Company and that for phosphorus was carried out by Alfred Microanalysis laboratory, West Germany. Chloride and bromide were determined by Volhard method⁽⁷⁾. Indium was determined as EDTA complex⁽²⁾. Melting points were measured using an ordinary Gallenkamp tube melting apparatus.

All chemicals used were of analytical grade reagents (A.R.), BDH, Merck, Sigma or extra pure grade. The organic ligands were prepared as previously mentioned⁸⁻¹⁰.

Results and Discussion

Re-investigation of the supposed complex of indium (III)⁽¹⁾, with triphenyl-phosphine $InCl_3 \cdot 2Ph_3P$, suggested that the complex is probably the phosphine oxide one. The reaction between triphenylphosphine and indium (III) in the presence of air gave triphenylphosphine oxide adduct. The complexes are similar to authentic samples prepared from indium trihalides and triphenylphosphine oxide in ethyl acetate, $InX_3 \cdot 2Ph_3PO$, and it seems

that slow oxidation of triphenylphosphine in presence of air had occurred. Similar results are reported-.

The addition of an ethanolic solution of MePh_3PI to a solution of InCl_3 in ethanol saturated with HCl gave a product of the type $\text{InCl}_3, 2\text{MePh}_3\text{PCI}$.

Carty and Tuck⁽¹⁾ reported the preparations of $\text{InX}_3, \text{DiPhOS}$ (where $\text{X} = \text{Br}$ or I and $\text{DiPhOS} = 1,2$ - bis (diphenyl-phosphino) ethane), but they were unable to prepare the corresponding chloride adduct. During this work we report the preparations of $\text{InCl}_3, \text{DiPhOS}$ and the indium trichloride adduct with DiPhOS oxide, $\text{InCl}_3, \text{DiPhOS}$ oxide. The reaction of ethanolic solutions of InX_3 and diphenyl sulphoxide, Ph_2SO , applying the mole ratio of 1:2 gave adducts analysed as $\text{InX}_3, 3\text{Ph}_2\text{SO}$. These adducts are recovered unchanged after boiling with ethanol. When a solution of InCl_3 in ethanol was added to dimethyl sulphoxide, Me_2SO , the adduct obtained proved by analysis to be $\text{InCl}_3, 4\text{Me}_2\text{SO}$. The same product was obtained without using any solvent and the excess of the ligand was pumped off at 60°C under reduced pressure.

Reaction of InCl_3 and bipyridly, bipy, in the mole ratio 1:1.5 gave a product similar to that previously reported⁽¹⁰⁾. On using excess of the ligand, five-fold, different product was obtained, $\text{InCl}_3, 2\text{bipy}, 3\text{H}_2\text{O}$. The adduct $\text{InCl}_3, 3\text{bipy}$, was reported by Sutton applying different method of preparation⁽¹¹⁾.

On mixing solutions of InCl_3 and organic compounds in the mole ratio of 1:2, adducts of the type $\text{InCl}_3, 1.5\text{L}$ (where $\text{L} = o\text{-phen.}, \text{DM-bipy}, \text{pyrazine}$) were obtained. The possible structure of such adducts with this unusual stoichiometry was discussed by Johnson and Walton⁽¹⁰⁾.

Monoadducts of the type InX_3, L (where $\text{L} = \text{DM-}o\text{-phen.},$ and $2,2',2''\text{-tripyridyl}$) were obtained on adding ethanolic solutions of indium trihalides to solutions of the ligands in the same solvent. No other adducts were obtained even on using excess of the ligand.

Reactions in the presence of HCl or HBr solutions using the mole ratio of 1:2, gave products proved by analyses and infrared

studies to have the general formula, $\text{InX}_3 \cdot 2\text{L} \cdot 2\text{H}_2\text{O}$ (where L = o-phen. or bipy.).

In the reactions of o-phenanthroline and bipyridyl with either InCl_3 or InBr_3 , it was found that a change in the reaction conditions brought about a change in the adducts obtained.

On using bulky ligands, the products obtained were the mono-adducts, $\text{InX}_3 \cdot \text{L}$ (where X = Cl or Br and L = 2,9-dimethyl-o-phenanthroline, and 2,2',2''-tripirydyl), m.p.s., yields and analytical data are given in Table I.

Infrared Measurement

The infrared spectra in the region 650–4000 cm^{-1} for indium (III) adducts are discussed. The coordinate bond in such type of complexes is predicted to be below 150 cm^{-1} (12).

As indicated in Table (2), shifts in the P = O stretching frequency occurs due to coordination to InX_3 (X = Cl or Br) through oxygen. This is in agreement with earlier reports. Coordination occurs through the oxygen atom in indium sulphoxide complexes. The split of the S-O bond in case of $\text{InBr}_3 \cdot 3\text{Ph}_2\text{SO}$ may be attributed to differently coordinated Ph_2SO molecules. The compound may be formulated as $\text{InBr}_3 \cdot 2\text{Ph}_2\text{SO} \cdot \text{Ph}_2\text{SO}$ Fig. 1. Similar behaviour of Ph_2SO complexes are reported₃₃.

The infrared spectra of the complexes $\text{InX}_3 \cdot n\text{L}$ (where X = Cl or Br and L = o-phen., DM-o-Phen., 2,2',2''-tripirydyl, 2,2'-bipy, and DM-Bipy.), show in general a change in the C-H bending frequencies in the range 860–730 cm^{-1} , and another change with multiple splitting in the region 1700–1400 cm^{-1} .

Conductivity Studies.— Conductivity measurements in non-aqueous solutions have frequently been used in structural studies of indium (III) complexes. Within the limits of the solubilities of the complexes prepared, we have measured the molar conductivities of millimolar solutions in organic solvents. The results are recorded in Table (3). From the table, it is clear that the solution of $\text{InCl}_3 \cdot \text{DM-o-Phen.}$, behaves as a weak electrolyte in the organic solvents used. The complex $\text{InCl}_3 \cdot \text{tripiry.}$ behaves as strong electrolyte in DMF (Fig. 1).

TABLE 1:

Compound	Found (%)				Required (%)							
	C	H	P/N	Halide Cl/Br	C	H	P/N	Halide Cl/Br	Yield %	M.P. °C		
In Cl ₃ , 2MePh ₃ Cl	53.4	4.1	7.1	13.3	20.8	53.9	4.3	7.3	13.6	21.0	86.6	130
In Cl ₃ , Diphos	49.0	4.4	—	18.2	17.0	50.4	3.9	—	18.5	17.2	82	231
In Cl ₃ , Diphos Oxide	—	—	—	17.4	16.35	—	—	—	17.6	16.34	72.9	>240
In Cl ₃ , 3 Ph ₂ SO	52.3	4.4	—	13.6	12.7	52.2	3.6	—	13.9	12.9	97.6	125
In Br ₃ , 3 Ph ₂ SO	46.1	4.4	—	11.8	25	45.0	3.2	—	11.9	24.9	94.4	110
In Cl ₃ , 4 DMSO	18.8	5.6	—	21.3	19.5	18.0	4.5	—	21.5	19.95	86.9	158
In Cl ₃ , dimethyl-o-phenanthroline	39.2	3.2	6.5	16.5	24.5	39.2	2.8	6.5	20.4	42.6	87.5	>240
In Br ₃ , dimethyl-o-phenanthroline	28.9	2.3	4.8	20.3	42.3	29.9	2.2	5.0	20.4	42.6	87.5	>240
In Cl ₃ , o-phenanthroline	34.5	3.2	6.2	28.4	26.2	35.9	2.0	6.7	28.6	26.5	93.	>240
In Cl ₃ , 1,5-o-phenanthroline	43.8	3.3	—	23.2	21.0	44	2.5	—	23.4	21.1	93.9	>240
In Cl ₃ , 2,0-phenanthroline dihydrate	46.7	3.5	—	18.5	17.1	46.6	3.6	—	18.6	17.2	91.7	>240
In Br ₃ , o-phenanthroline.	27.0	2.8	—	21.45	44.5	26.95	1.5	—	21.5	44.8	98.2	>240
In Br ₃ , 2,0-phenanthroline·2H ₂ O	38.3	3.1	6.7	15.3	31.65	38.4	2.7	6.4	15.3	31.9	80.9	>240
In Cl ₃ , 1,5 (2,2-bipyridyl), H ₂ O	37.5	4.2	—	24.1	22	38	3	—	24.3	22.5	94.6	>240
In Cl ₃ , 2 (bipyridyl), 3H ₂ O	40.2	3.9	—	19.35	17.7	40.8	3.8	—	19.5	18.1	93.6	>240
In Cl ₃ , 2(2,2-bipyridyl), 2H ₂ O	41.9	3.8	9.8	22.2	18.8	42.2	3.5	9.8	20.2	18.7	98.7	240
In Cl ₃ , 1,5 (dimethyl-2,2-bipyridyl)	43.9	4.3	8.1	20.8	21.0	43.5	3.5	8.4	23	21.4	93.4	245
In Br ₃ , DM-bipy., EtOH	28.6	3.9	—	19.5	40.5	28.8	3.1	—	19.6	40.9	93.9	245
In Cl ₃ , 2,2', 2'',-tripyridyl).	39.9	3.1	8.2	25.1	23.1	39.6	2.4	9.2	25.3	23.4	81	>240
In Br ₃ , 2,2',2'',-tripyridyl).	31.3	2.7	—	19.4	40.4	30.7	1.9	—	19.5	40.8	94	>240
In Cl ₃ , 1,5 (Pyrazine).	21.7	2.4	—	33.5	30.8	21.1	1.8	—	33.6	31.1	93.6	>240
In Br ₃ , 2 (Pyrazine).	18.4	2.4	—	22.1	46	18.6	1.6	—	22.2	46.6	97.3	>240

* Low carbon value was obtained.

Table 2: Infrared Spectra

Compound	cm ⁻¹	Δv (cm ⁻¹)	Ref.
Ph ₃ PO	1195	—	8
InCl ₃ , 2Ph ₃ PO	1170	25	
InBr ₃ , 2Ph ₃ PO	1170	25	
DiPhOS oxide	1190	—	9
InCl ₃ , DiPhOS oxide	1160	35	
Ph ₃ SO	1040	—	13
Me ₃ SO	1055	—	
InCl ₃ , 3Ph ₂ SO	970	70	
InBr ₃ , 3Ph ₂ SO	980	60	
	960	80	
InCl ₃ , 4Me ₂ SO	1040	15	

Table 3: Conductivities in Different Solvents

Compound	— o Ohm ⁻¹ Cm ¹			
	Acetonitrile (150) ¹¹	PhNO ₂ (20-40) ¹¹	MeNO ₂ (70-120) ¹¹	DMF (70-100)*
MePh ₃ Pl	—	—	—	60-100*
InCl ₃ , 2(o-Phen.), 2H ₂ O	—	—	—	83
InBr ₃ , 2(o-Phen.), 2H ₂ O	—	—	—	83
InCl ₃ , 1.5(o-Phen.)	—	—	—	W
InBr ₃ , 1.5(o-Phen.)	—	—	—	W
InCl ₃ , DM-o-Phen.	W	W	—	W
InBr ₃ , DM-o-Phen.	W	W	—	W
InCl ₃ , 1.5(bipy.) H ₂ O	W	—	W	—
InCl ₃ , 2(bipy), 2H ₂ O	W	W	W	—
InBr ₃ , 1.5 (bipy.)	W	30.6 (s)	W	—
InCl ₃ , 1.5 (DM-bipy.)	W	—	—	—
InBr ₃ , (DM-bipy.), EtOH	151 (s)	—	—	—
InCl ₃ , 2,2', 2''-tripy.	—	—	—	104 (s)
InBr ₃ , 2,2', 2''-tripy.	—	—	—	W

* Values for the molar conductivities of millimolar solution of 1:1 electrolytes in these solvents.

Where s = strong and W = Weak electrolytes.

Table 4: Molecular Weights Determinations of some Indium (III) Complexes

Compound	Mobs	Mcal	F	Solvent
InCl ₃ , 2Ph ₃ PO	135	777.83	5.76	DMF
InBr ₃ , 2Ph ₃ PO	188	911.15	4.85	DMF
InCl ₃ , o-Phen.	200	401.4	2	DMF
InCl ₃ , 1.5-o-Phen.	434	491.5	1.1	DMF
InCl ₃ , 2-o-Phen., 2H ₂ O	212	617.65	2.9	DMF
InBr ₃ , o-Phen.	270	543.7	1.9	DMF
InBr ₃ , 1.5-o-Phen.	454	624.86	1.38	DMN
InBr ₃ , 2-o-Phen., 2H ₂ O	227	750.97	3.3	DMF
InCl ₃ , DM-o-Phen.	229	429.46	1.88	DMF
InCl ₃ , 2,2', 2''-tripy.	294	454.44	1.55	DMF
InBr ₃ , 2,2', 2''-tripy.	227	587.81	2.6	DMF
InCl ₃ , 1.5-bipy., H ₂ O	380	491.5	1.3	Acetonitrile
InCl ₃ , 2-bipy., 2H ₂ O	208	569.57	2.7	Acetonitrile
InBr ₃ , 1.5-bipy.	212	588.8	2.7	Acetonitrile
InCl ₃ , 1.5-DM-bipy.	450	497.55	1.1	Acetonitrile
InBr ₃ , DM-bipy., EtOH	493	556.7	1.13	Acetonitrile

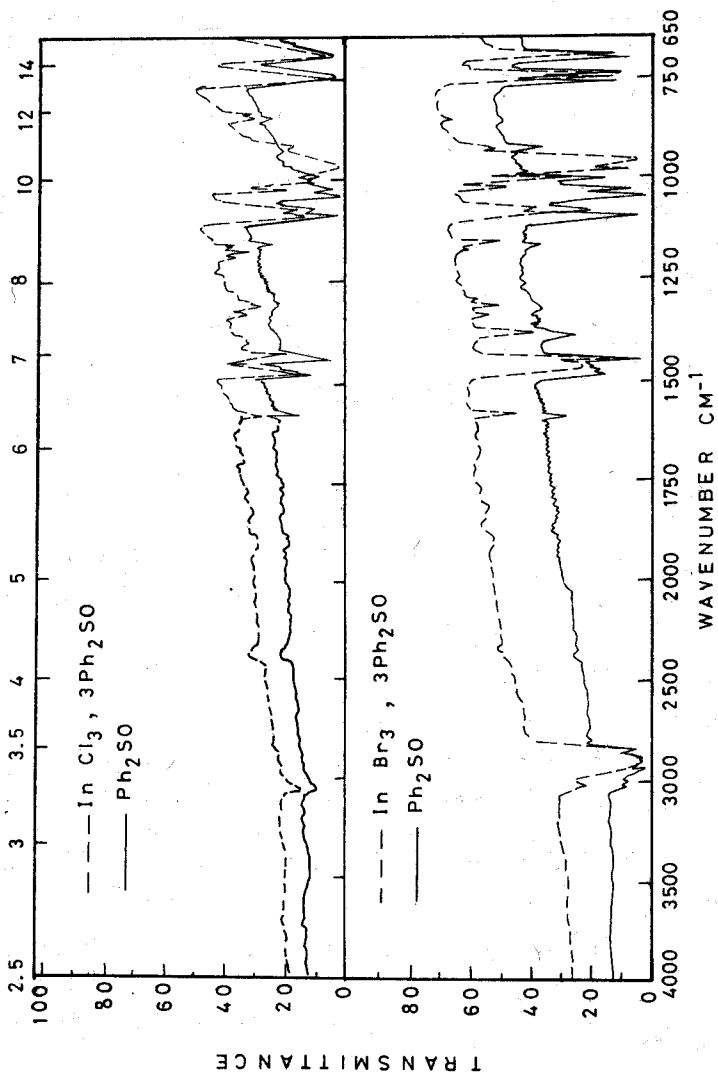


Fig.(1) The infrared spectra of diphenyl sulphoxide adducts.

Molecular Weights. The molecular weights of some adducts of indium trichloride and tribromide have been determined in DMF and acetonitrile (Table 4).

The dissociation factors, F , show that the addition compounds $\text{InCl}_3 \cdot 1.5L$ ($L = o\text{-Phen.}, \text{DM-bipy.}$) and $\text{InBr}_3 \cdot \text{DM-bipy}$

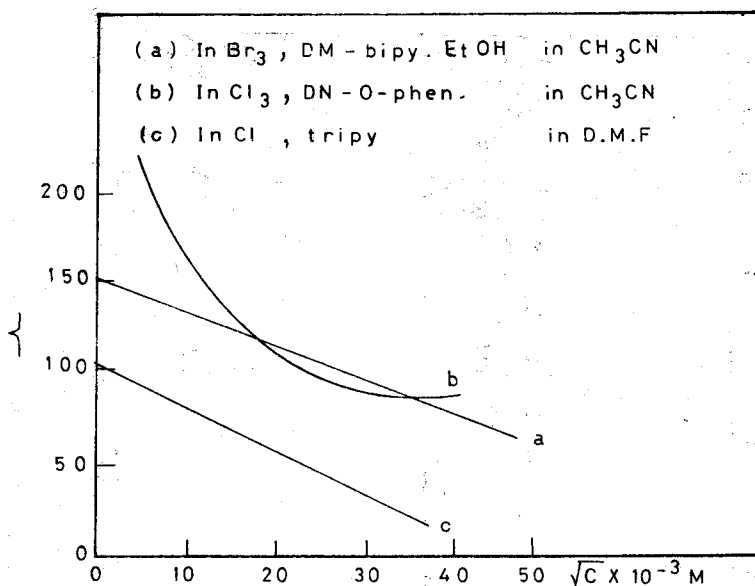


Fig. (2) The relationship between the conductivity and conc. of some indium (III) complexes.

EtOH are all monomers within the limits of the experimental error. Apart from these adducts, all the other indium trichloride and tribromide complexes undergo some dissociation in organic solvents. This lability is presumably due to the comparable stabilities of 4-, 5-, and 6- coordinate states of indium (III).

The overall conclusion from these studies is that the molecular weight determination imply a more complete dissociation than do the conductometric results for the indium (III) complexes. Similar results are reported.

Thermal Stability.- The compound $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ was reported to lose 2 moles of water at 100°C ; whereas $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ was said to be dehydrated completely at this temperature. Thermogravimetric analysis of $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ shows that a complex series of changes occur on heating which were illustrated by the equations

Table 5: Thermal Decomposition of Some Indium (III) Complexes

Temp. (°C.)	Mobs.	Formula	Mcal.
InCl ₃ , 3H ₂ O			
25 - 200 °C	275.2 - 212.1		275.22 - 212.1
200 - 300	207	In(OH) ₂ Cl, H ₂ O (A)	202.3
300 - 440	185.0	In(OH) ₂ Cl (B)	184.3
440 - 460	110	In	114.8
In(NO ₃) ₃ , 5H ₂ O			
25 - 105 °C	390.8 - 370	In(NO ₃) ₃ , 4H ₂ O (I)	372.8
140 - 165	262	In(NO ₃) ₂ O ₂ H ₂ O (II)	264
165 - 200	188	InO(NO ₃) (III)	192
InBr ₃ , 2Ph ₃ PO			
25 - 200 °C	911.1	InBr ₃ , 2Ph ₃ PO	911.1
400	110	In (c)	114.8
InCl ₃ , 3Ph ₂ SO			
25 - 200	828 - 813	InCl ₃ , 3Ph ₂ SO	828
550 °C	163	InOCl	165.5
InCl ₃ , 4DMSO			
25 - 100	533.47	InCl ₃ , 4DMSO	533.47
350 - 450	2.10	InCl ₃ (d)	221.1
550 - 800	170	InOCl (E)	165.5
InCl ₃ , 1.5(o-phen)			
25 - 450	491.5 - 398.5	InCl ₃ , o-phen	491.5 - 401.4
750	—	Volalite	—
InCl ₃ , 2(o-phen)2H ₂ O			
25 - 200	617.65	InCl ₃ , 2(o-phen) 2H ₂ O	617.65
770	580	InCl ₃ , 2(o-phen)	581.65
750	170	InOCl (f)	165.5
InBr ₃ , 2-o-phen, 2H ₂ O			
25 - 200	750.97	InBr ₃ , 2-o-phen, 2H ₂ O	750.97
300	713.4	InBr ₃ , 2-o-phen, (G)	714.97
750	112	In (H)	114.82
InCl ₃ (DM-o-phen)			
25 - 400	429 - 395	InCl ₃ (DM-o-phen).	429
750	110	In (I)	114.8
InBr ₃ , (2,2,2''-tripy)			
25 - 300	587.81	InBr ₃ (2,2,2''-tripy)	587.81
650 - 800	118	In (j)	114.8
InCl ₃ (2,2,2''-tripy)			
25 - 300	454.5	InCl ₃ , 2,2,2''-tripy	454.5
650	210	InCl ₃ (k)	221.19
InCl ₃ , 1.5 bipy, H ₂ O			
25 - 100	473.47	InCl ₃ , 1.5 bipy, H ₂ O	473.47
700 °C	175	InOCl (L)	165.5
InCl ₃ , 2(bipy) 3H ₂ O			
25 - 200	587.6	InCl ₃ , 2bipy, 3H ₂ O	587.6
350	520	InCl ₃ , 2bipy, (M)	516
600	270	In ₂ O ₃ (N)	277
InCl ₃ (bipy) ₂ , 2H ₂ O			
25 - 100 °C	569.57	InCl ₃ , 2 (bipy) 2H ₂ O	569.57
200	533.97	InCl ₃ , 2 bipy (O)	533.57
240 - 300 °C	462.8	InCl ₃ , 1.5. bipy (P)	455
450 - 500 °C	320.4	InOCl, bipy (Q)	321.7
600 °C	275.9	In ₂ O ₃	277
(InBr ₃ , 1.5 bipy)			
25 - 100 °C	588.8	InBr ₃ , 1.5 bipy	588.8
700	—	Volatile.	—
InBr ₃ , DM-bipy EtOH			
25 - 100 °C	584.8 - 570	InBr ₃ , DM-bipy, EtOH	584.8
200 - 300 °C	533	InBr ₃ , DM-bipy (R)	538.8
650 °C	215	InOBr (S)	211
InCl ₃ , 1.5 (DM-bipy)			
25 - 100	497.5 - 486.7	InCl ₃ , 1.5 (DM-bipy).	497.55
300 - 400	405	InCl ₃ , DM-bipy. (T)	405.4
650 °C	160	InOCl	165.5

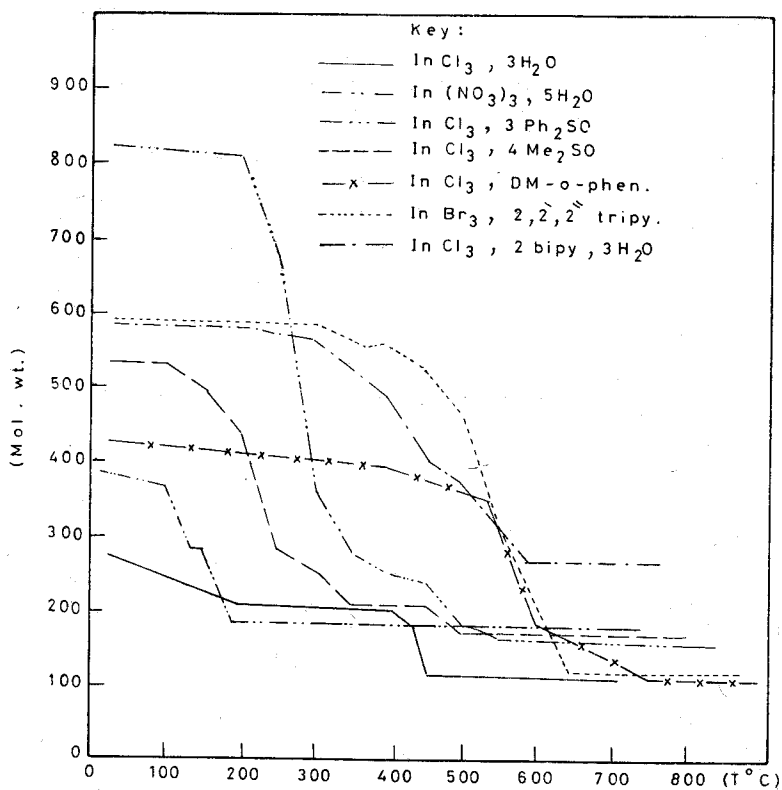
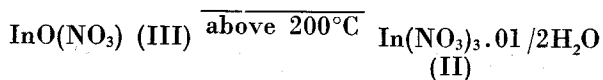
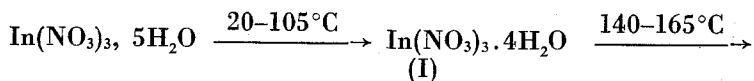


Fig. (3) Thermal decomposition of some indium (III) complexes.



The final product is indium oxynitrate.

The present work shows that indium (III) compounds decompose on heating up to 800°C. The molecular weights of the intermediate compounds are calculated from the graphs. The final products, as indicated in Table 5, are usually In, In₂O, InOX (X = Cl or Br), or InO (NO₃) as shown in Fig. 3.

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