

The Interaction of Indium(III) with Some Lewis Bases Containing Oxygen and Nitrogen as Their Potential Sites of Donation

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In the present paper the authors report the synthesis and characterization of cationic In^{3+} complexes of some Lewis bases containing oxygen and nitrogen donor sites.

INTRODUCTION

Indium(III) perchlorate hydrate reacts with a variety of donor ligands containing nitrogen atoms, to give adducts having a complex cation and perchlorate anion of type $(\text{InL}_3)(\text{ClO}_4)_3$ where L = bipyridyl, *o*-phenanthroline and ethylenediamine¹.

A number of addition compounds of indium perchlorate with organic bases containing oxygen donor atom have been reported *e.g.* urea,² dimethyl sulphoxide^{3,4} and N,N-dimethyl acetamide.⁵⁻⁷ Each of these three products involves six-coordinate indium(III), but the product obtained with triphenylphosphine oxide was reported^{3,4} to have the formula $\text{In}(\text{Ph}_3\text{PO})_4(\text{ClO}_4)_3$. As indicated from the infrared spectroscopic studies, coordination in all these complexes occurs through the oxygen atom. Carty and Tuck¹ reported that indium(III) possesses the coordination number four in its complexes with triphenylphosphine and triphenylarsine, $\text{In}(\text{Ph}_3\text{P})_4(\text{ClO}_4)_3$ and $\text{In}(\text{Ph}_3\text{As})_4(\text{ClO}_4)_3$, respectively. Evidence for four- and six-coordinate cationic and neutral indium(III) species was reviewed¹. There is a variety of complexes⁹⁻¹³ of indium(III) but little work has been done on cationic complexes. Carty and Tuck¹⁰ reported the properties of some complexes of $\text{In}(\text{ClO}_4)_3$ and donor ligands. The present paper is concerned with the preparations of cationic In^{3+} complexes and investigation of some of their properties.

Experimental

Indium(III) perchlorate hydrate, $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ was obtained by dissolving the metal in hot aqueous perchloric acid, reducing the volume of solution by

evaporation, and allowing the white deliquescent solid to crystallise. Excess of acid was removed by vacuum. Some of the organic ligands used were prepared as previously described^{14,15}; others were reagent-grade materials, and were recrystallised before use. Solvents were dried by conventional methods¹⁶.

Indium was determined by titration with EDTA, pyridine-2-azo-4-resorcinol being used as indicator¹³. Complexes were generally dissolved in 8 M aqueous hydrochloric acid, and the pH of the solution adjusted to 8–10; precipitated indium hydroxide was dissolved by adding 1 M sodium potassium tartrate. The colour change of the indicator, normally rather slow, could be accelerated by heating the wet solution to 60°C. Other analyses were made by conventional micro-methods, except that carbon was determined by the wet oxidation method because of the explosive nature of the complex perchlorates; this was carried out by Alfred Microanalytical Laboratory, West Germany.

Infrared spectra were measured using Perkin-Elmer 1430. Calibration of frequency reading was made with a polystyrene film. Conductivities were measured using a Beckman electronic switchgear model RA-2A with balance indicator. The pH of solutions, for the quantitative analysis of indium, was adjusted using a Pye Unicam pH meter type 292.

Preparation of the complex compounds: Tris(4,4'-DM-bipy) indium(III)

A solution of indium perchlorate hydrate (1 mmole), was added to a solution of 4,4'-DM-bipy. (4 mmoles) in the same solvent. The white powdery product obtained was filtered, washed with ether and dried, m.pt. > 240°. (Found: C, 43.9; H, 3.1; N, 8.2; In, 11.5. $\text{In}(\text{ClO}_4)_3 \cdot 3\text{C}_{12}\text{H}_{12}\text{N}_2$ requires: C, 44.7; H, 3.8; N 8.7; In, 11.9%). The excess unreacted ligand, m.pt. 168°C, was recovered from the filtrate. DM-bipy. was extracted with chloroform from an alkaline solution of the complex, and then determined¹⁷ spectrophotometrically at 281 nm (Found: DM-bipy., 56.4%. Calc.: 57.2%). The compound is insoluble in most organic solvents and decomposes in aqueous acid or alkali.

Tris(DM-*o*-phen.) indium(III) perchlorate

The reaction of DM-*o*-phen. (4 mmoles) with indium(III) perchlorate carried out under the same conditions as those used for the DM-bipy. complex gave a white powdery product. (Found: In, 10.7. $\text{In}(\text{ClO}_4)_3 \cdot 3\text{C}_{14}\text{H}_{12}\text{N}_2$ requires: In, 11.1%). The DM-*o*-phen. in the complex was determined spectrophotometrically at 270 nm. (Found: DM-*o*-phen. 59.6% Calc.: 60.2%). (experimentally In : DM-*o*-phen. ratio 1 : 3.09). The solubility of this compound was very similar to that of the DM-bipy. complex.

Bis(tripy) indium(III) perchlorate

This complex was obtained as a white powder by a method reported previously¹ and was prepared in this work for comparison. The tripy. content in this adduct

was determined spectroscopically, by using the broad absorption band,¹ centered¹⁸ at 280 nm, the complex was decomposed by aqueous sodium hydroxide and the tripy. extracted with chloroform [requires: tripy., 53.0; In, 13.05% Found: tripy. 53.6; In, 12.6 In(tripy.)₂(ClO₄)₃].

Bis-(Diphos methane) indium(III) perchlorate

When a solution of the ligand, 4 mmoles, in ethanol was added to a solution of indium(III) perchlorate, 1 mmole, in the same solvent, a white powdery product was obtained, which was filtered and dried. [Found: C, 49.9; H, 4.3; In, 9.01. In(ClO₄)₃·2C₂₅H₂₂P₂ requires: C, 50.8; H, 3.8; In, 9.7%.]

Excess ligand was recovered on concentrating the filtrate, m.pt. 114°C.

When similar procedure was followed using diphos methane dioxide as a ligand, the complex obtained was bis(diphos methane dioxide) indium(III) perchlorate. [Found: C, 47.5; H, 3.1; In, 9.9. In(ClO₄)₃·2C₂₅H₂₂P₂O₂: requires: C, 48.2; H, 3.6; In, 9.2%.]

Bis(diphos ethane) indium(III) perchlorate

This complex was obtained as white solid on mixing solutions of the two reactants in ethyl acetate. Recrystallisation from nitromethane caused slight change in the complex. [Found: C, 1.0; H, 4.6; In, 9.2. Calcd. for In(ClO₄)₃·2C₂₆H₂₄P₂: C, 51.6; H, 4.0; In, 9.5%.]

Bis(diphos ethane dioxide) indium(III) perchlorate

When solutions of the two reactants in ethanol, in the mole ratio of L : In (ClO₄)₃ as 2 : 1 were mixed, the corresponding dioxide adduct was obtained as air-stable product [Found: C, 50.1; H, 3.2; In, 8.6. In (ClO₄)₃, 2C₂₆H₂₄P₂O₂ requires: C, 49.0; H, 3.8; In 9.0%].

Determination of indium by titration with EDTA, in the case of the complexes containing phosphorus proved unsuccessful, apparently because the phosphorus oxoanions present, after decomposition with aqua regia or fusion with sodium hydroxide obscured the end point; check titrations with standard indium solutions in the presence of phosphate ion gave low results. In these complexes, indium was determined gravimetrically by dissolving the complex in ethanol and precipitation of the bis-tripy. complex.

Tetrakis (Ph₂SO) indium(III) perchlorate

Ph₂SO (4 mmoles) in ethanol and indium(III) perchlorate (1 mmole) were refluxed in ethanol, ether was then added to the cold reaction mixture. On standing a white crystalline product was formed which was filtered off and dried. [Found: C, 46.3; H, 2.8; In, 9.0. In(ClO₄)₃·4C₁₂H₁₀SO requires. C, 47.2; H, 3.3; In, 9.4%.]

Tetrakis (py. N-oxide) indium(III) perchlorate

This complex was obtained on adding a solution of py. N-oxide (4 mmoles) in ethanol to a solution of indium(III) perchlorate (1 mmole) in the same solvent. The product obtained was washed several times with ethanol and filtered off. [Found: C, 29.4; H, 3.0; In 13.9. In $(\text{ClO}_4)_3$, $4\text{C}_5\text{H}_5\text{NO}$ requires C, 30.3; H, 2.6; In, 14.5%.]

Bis(diphenyl sulphophosphino) methane or diphenyl sulphide gave no complexes by the previous procedures. This is in confirmation with the other findings¹⁴

RESULTS AND DISCUSSION

The most important feature of the complexes studied is that the perchlorate exhibits a single strong band centred at 1105 cm^{-1} , characteristic of ionic perchlorate; the band at 920 cm^{-1} , assigned for coordinated perchlorate¹⁹, was not observed.

Changes were observed in the infrared spectra of the organic ligand on complexing with In^{3+} . With DM-bipy. and DM-phen., there are multiple splittings in the regions $725\text{--}850\text{ cm}^{-1}$ and $1600\text{--}1540\text{ cm}^{-1}$. Similar changes have been reported²⁰ for other DM-bipy. complexes. The infrared spectra of the complexes formed between $\text{In}(\text{ClO}_4)_3$ and diphos methane or -ethane are very similar to that of the ligands.

In the complexes of diphos methane dioxide and diphos ethane dioxide, shifts of *ca.* 60 and *ca.* 65 cm^{-1} , respectively were observed for the $\text{P} = 0$ stretching band of the free ligand at 1195 cm^{-1} . This indicates that bonding to indium is through oxygen²¹. Similarly in the complexes $\text{In}(\text{Ph}_2\text{SO})_4(\text{ClO}_4)_3$ the $\text{S}=\text{O}$ stretching frequency was at 970 cm^{-1} , a reduction of 70 cm^{-1} from the uncomplexed ligand (1040 cm^{-1} vs.), indicating coordination to the oxygen atom^{3,4}. The frequency of the $\text{N}-\text{O}$ group in pyridine N-oxide occurs⁹⁻²² at 1180 cm^{-1} and shifts to 1195 cm^{-1} in its complex indicating that coordination is through the oxygen atom. Similar results were reported.²³

Among the factors affecting the coordination number of In^{3+} in the complexes obtained during the present work is steric effect and this explains the lowering of the coordination number in some complexes. Other explanation is that the 4-coordination of In^{3+} only occurs with ligands that can form both σ - and π -bonds with the metal.

The conductivities of the complexes were measured in nitromethane and are given in Table 1. The observed conductivities are lower than those expected for 1 : 3 electrolytes ($390\text{ ohm}^{-1}\text{cm}^2$) in nitromethane²⁴. This may be attributed to the partial decomposition of the complexes in solution. Sutton *et al.*²⁵ reported molar conductivities in the range $180\text{--}190\text{ ohm}^{-1}\text{cm}^2$ for some indium(III) halide

complexes in the same solvent. It is likely that such low conductivities may be a general feature of nitromethane solutions of indium complexes.

TABLE 1
CONDUCTIVITIES IN NITROMETHANE

Compounds	Ω_0 (ohm ⁻¹ cm ²)
In(DM-bipy.) ₃ (ClO ₄) ₃	243
In(DM-phen.) ₃ (ClO ₄) ₃	230
In(tripy.) ₂ (ClO ₄) ₂	241
In(Diphos methane) ₂ (ClO ₄) ₃	305
In(Diphos methane dioxido) ₂ (ClO ₄) ₃	265
In(Diphos ethane) ₂ (ClO ₄) ₃	315
In(Diphos ethane dioxido) ₂ (ClO ₄) ₃	352
In(Ph ₂ SO) ₄ (ClO ₄) ₂	360

Where

DM-Bipy = 4, 4'-dimethyl-2, 2'-bipyridyl,

DM-phen = 2,9-dimethyl-4,4'-phenanthroline

tripy. = 2,2',2''-dtipyrindyl,

Disphos methane = diphenylphosphino methane.

Ph₂SO = diphenyl sulphoxide, and

py. N-oxide = pyridine N-oxide.

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