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Physico-Chemical Studies on Some Mixed Ligand Hydrido-phosphine Complexes of Ir(III) with Ethylene Thiourea.

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Some mixed ligand hydrido-phosphine complexes of Ir(III) with ethylene thiourea have been prepared and investigated using various physico-chemical techniques. Ethylene thiourea forms stable coloured complexes depending on the conditions of the reaction. The systematic shift in the four thioamide bands of ethylene thiourea in the IR spectra indicate its bonding through thiocarbonyl sulphur. The ligand field bands of complexes are obscured by charge transfer band in the electronic spectra. Tentative octahedral configuration of all complexes have been assigned.

INTRODUCTION

Organometallic compounds of iridium are of special interest due to their valuable catalytic applications for hydrogenation of organic reactions and being more efficient homogeneous catalyst than rhodium analogue[1]. Catalytic activity of some iridium (III) phosphine complexes have also been studied by Nicholson *et al*[2]. The present study is undertaken with a view to prepare and investigate some mixed ligand hydrido-phosphine complexes of Ir(III) with ethylene thiourea (ETU).

EXPERIMENTAL

All chemicals used were of AR or CP grade. Ethylene thiourea was prepared by the method of Allen *et al*[3].

Preparation of Complexes

$IrCl_3 \cdot xH_2O$ (0.05 mol), KCl (0.05 mol) and triphenyl phosphine (0.6 mol) were suspended in 100 ml ethanol and stirred on magnetic stirrer for 2 h at 100°C in a covered beaker. The mixture was then evaporated on water-bath about 20 ml and desired molar ratio of ethylene thiourea in 20 ml benzene mixed with them and further stirred for 2 h at 85°C. The solution mixture was then allowed to evaporate on water-bath. In the residue two drops of conc. HCl was added and various coloured complex was obtained for each molar ratio of ethylene thiourea. The solid residue was mixed with methanol and few drops of benzene when excess of triphenyl phosphine was dissolved. It was then filtered, washed with methanol and dried in a vacuum desiccator over anhydrous $CaCl_2$. The analytical and physical data of complexes are given in Table 1.

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF IRIDIUM (III) COMPLEXES

Compd./Colour	Decomp. Temp.(°C)	Analysis % Found/(Calcd)					ΛM* $\Omega^{-1}cm^2mole^{-1}$
		C	H	N	Ir	Cl	
$[IrH_2(P\phi_3)_2(ETU)Cl]$	180	54.3	4.3	3.4	22.1	—	5.05
(Yellow)		(54.7)	(4.4)	(3.2)	(22.4)	—	
$[IrH(P\phi_3)_2(ETU)_2Cl]Cl$	182	50.6	4.4	5.5	19.4	7.3	53.02
(Light Pink)		(50.8)	(4.3)	(5.6)	(19.3)	(7.1)	
$[IrH(P\phi_3)(ETU)_4]Cl_2$	172	38.1	4.2	11.6	22.3	7.5	160.32
(Vellum)		(38.5)	(4.2)	(11.9)	(22.5)	(7.6)	
$[IrH_2(P\phi_3)_2(ETU)_3]Cl$	168	40.4	4.3	10.5	24.2	4.4	65.04
(Light Buff)		(40.6)	(4.3)	(10.2)	(24.3)	(4.3)	
$[Ir(P\phi_3)(ETU)_2Cl_3]$	110 d	37.5	3.5	7.0	25.0	13.8	18.70
(Light Biscuit)		(37.6)	(3.5)	(7.3)	(25.2)	(13.9)	

*At 30°C in 10^{-3} M DMF

RESULTS AND DISCUSSION

Iridium(III) is a B-class acceptor forms stable complexes with soft-ligand like triphenyl phosphine. The abstraction of hydride ligand occurs from ethanol leading to the formation of hydrido-phosphine complex. The hydrido-phosphine complex reacts with ETU giving various products. The molar ratio of ETU controls the formation of all products. When stoichiometry of Ir and ETU was 1 : 2, mixture of three different products was formed, from which each one was separated. All products obtained were diamagnetic indicating $T_{2g}^{6}e_{g}^{0}$-configuration of d^6-ion (Ir^{3+}). Molar conductance (10^{-3} M) of $[IrH_2(P\phi)_3(ETU)Cl]$ and $[Ir(P\phi_3)$-$(ETU)_2Cl_3]$ complexes were found to be less than 10 $\Omega^{-1}cm^2mole^{-1}$ suggesting their non-electrolytic nature. But molar conductance value of other complexes suggest the presence of ionic chloride which is further supported by the chemical analysis of their Na_2CO_3 extract. When these complexes were shaken with aquous Na_2CO_3 solution thoroughly and the aqueous extract was filtered, acidified with dil HNO_3 and when treated with $AgNO_3$ gave precipitation of chloride as AgCl. However, the total chlorine as AgCl was only obtained in case of $[IrH(P\phi_3)(ETU)_4]Cl_2$.

Electronic spectra of $[IrH(P\phi_3)_2(ETU)_2Cl]Cl$ and $[IrH_2(P\phi_3)(ETU)_3]Cl$ display only a single very strong broad band between 266–226nm, and 264–234nm region respectively. The other ligand field bands are obscured. However, other complexes contain three bands at 222, 249 and 279 nm in $[Ir(P\phi_3)(ETU)_2Cl_3]$, at 219, 248 and 281nm in $[IrH(P\phi_3)(ETU)_4]Cl_2$ and at 236, 260 and 292nm in $[IrH_2(P\phi_3)_2(ETU)_2]$. The first band is entirely of charge transfer origin and the other two bands are due to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transition having some contributions from charge transfer. Thus, octahedral configuration may be assumed in accordance with known preference of six-coordinated Ir(III) ion[4–6].

The IR spectrum of $P\phi_3$ molecule is recorded and interpreted by Deacon *et al*[7] and ETU molecule by Meck and co-workers[8]. Agarwala and Rao[9] have also performed normal coordinate analysis of ETU. A comparison of the spectra of complexes with those of ETU in Table 2 indicate that metal-sulphur bonding results in a decrease in the frequency of thioamide band IV by 15–25 cm^{-1}. Band I and Band II remains almost identical, Band III is either considerably lowered in intensity and/or experiences a red shift to lower frequency of the order of 25 ± 5 cm^{-1}. The systematic shift of four thioamide bands of ETU clearly suggest bonding of ETU through thiocarbonyl sulphur.[10–13] The νNH band of ETU (*ca.* 3250 cm^{-1}) blue shifts in all complexes indicating absence of bonding through imino nitrogen.

All hydrido-complexes display very low position of ν(Ir-H) probably due to *trans* influence of $P\phi_3$ molecule. The metal chlorine stretching bands are observed as weak bands at *ca.* 240 and 230 cm^{-1} in $[IrH_2(P\phi_3)_2(ETU)Cl]$ and at *ca.* 260 and 250 cm^{-1} in $[IrH(P\phi_3)_2(ETU)_2Cl]Cl$. So, considering the Ir-Cl stretching modes, it appears that $P\phi_3$ is *trans* to chlorine in $[IrH(P\phi_3)_2(ETU)_2Cl]$ and hydrogen is *trans* to chlorine in $[IrH_2(P\phi_3)_2(ETU)Cl]$ in most probable structure. Jenkins *et al*[14] and others[15] have suggested similar observations. The ν(Ir-P) (*ca.* 390 ± 5 cm^{-1}) and ν(Ir-S) (*ca.* 220 ± 3 cm^{-1}) modes are also in agreement with previous literature[16,17].

TABLE 2
ASSIGNMENT OF MAJOR SELECTED IR BANDS (cm^{-1}) OF ETU AND METAL COMPLEXES

Compound	νN-H (πNH)	Thioamide Bands#				ν Ir-H/ (δ Ir-H)	ν Ir-P/ (ν Ir-S)	ν (Ir-Cl) ——
		Band I	Band II	Band III	Band IV			
ETU	3250 s (590 m)	1530 s	1200 s	1040 s	685 s	—	—	—
$[IrH_2(P\phi_3)_2(ETU)Cl]$	3300 m (610 s)	1530 s	1190 m	1040 w	665 m	1860 m 1830 m (750 m)	390 m (212 w)	240 m (230 w)
$[IrH(P\phi_3)(ETU)_2Cl]Cl$	3265 s (570 m)	1530 s	1200 m	1225 w	670 m	1840 m (720 m)	380 m (230 w)	260 m 250 m
$[IrH(P\phi_3)(ETU)_4]Cl_2$	3260 sb (590 m)	1530 s	1200 m	1030 w	660 m	1825 m (750 m)	395 m 2351 w (210 w)	—
$[IrH_2(P\phi_3)(ETU)_3]Cl$	3300 sb (610 m)	1525 s	1200 m	920 m	670 m	1845 m 1835 m (700 m)	385 m (230 w 210 w)	—
$[Ir(P\phi_3)(ETU)_2Cl_3]$	3265 s (600 m)	1530 s	1200 m	1020 w	665 w	—	385 m (225 w)	350 w 340 w

#Mixed bands,

Band I has contribution from 60% $\delta_{sym.}$ NH + 20% $\nu_{sym}C - N$

Band II has contribution from 30% ν_{sym} C – N + 36% ν C= S + 24% δ_{sym} (NH)

Band III has contribution from 34% ν_{sym} $CH_2 - N$ + 34% νC – C + 26% C = S

Band IV has contribution from

46% νC – N + 30% $\nu C \cdots S$ + 11% sym. ring deformation.

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