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SYNTHESIS, CHARACTERIZATION AND ANTI-BACTERIAL STUDIES OF SOME LOW-VALENT ORGANOMETALLIC DERIVATIVES OF Pd (0), Pt (0), Rh (I) AND Ir (I) WITH 2-THIOBARBITURIC ACID

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ABSTRACT

Synthesis, charactersation and anti-bacterial studies on some low-valent orgenometallic derivalives of pd(o),pt(0),Rh(1) and Ir(1) ligated with 2-thiobarbituric acid are Investigated and strutural elucidation and anti-bacterical studies are elaborated. The structure of new complexes are deduced using elemental analysis,conductometric, magnetic mesurement,IR ,UV –vis ,`HNMR spectral data. Tetrahedral structure for pd(o)&Pt(0) and square planar structure for Rh(1) and Ir(1) complexes are tentatively assigned. The ligend and metal complexes are screened for their anti –microbial activity against gram negative bacteria, **E.coli** and gram positive bacteria **S.aureus.** The results indicated that complexes are active than free ligand.

Keywords : Low-valent, pt-metales ,spectra bio-activety ,Thioamide.

INTRODUCTION

Thiobarbituric acid (HTBA) is well known reagent in use for the determination of the lipid peroxidation in biological system[1-2] and pharmacological and analytical fields[3-5]. This molecule is used as ligand for complexes of transition metals[6-8]. However, the literature survey reveals that complexes of low-valent Pd (0), Pt (0), Rh (I) and Ir (I) are not reported incorporating triphenylphosphine or triphenylarsine. So, in continuation of our earlier work[9-12], we report synthesis, spectral characterization and reactivity of some new organometallic derivatives of Palladium (0), Platinum (0), Rhodium (I) and Iridium (I) ligated with thiobarbituric acid. All the synthesized compounds were tested against gram positive bacteria S.aureus and gram negative bacteria E-coli.

EXPERIMENTAL

All chemicals used were of Anal R or chemically pure grade. The precursor complexes, $[M(E\phi_3)_4]$ (E = P/As; M = Pd/Pt), $[Rh(P\phi_3)_3Cl]$, $[M(CO)(P\phi_3)_2Cl]$, (M = Rh/Ir) are prepared by the methods reported in literature[13-16]. All new complexes were prepared in benzene using precursors and thiobarbituric acid following our previous method reported in literature[17-19] and their analytical data is given in table 1. Elemental analysis was performed by the micro-analytical section RSIC, CDRI, Lucknow. IR spectra of ligand and complexes were recorded on a Perkin-Elmer 577 spectrometer in the range of 4000-200 cm^{-1} as KBr pellets and electronic spectra on a Beckmann Du6 spectrophotometer. The molar conductance (10^{-3} M) of complexes were measured in DMF using Wiss-Wekstatter Weitheim obb type LBR conductivity meter. The magnetic measurements were made on a gouy balance. 1H NMR spectra of ligands and complexes were obtained with Varian EM 390 MHz NMR spectrophotometer.

RESULTS AND DISCUSSION

All solid products were isolated by ligand substitution reactions in benzene. All $P\phi_3/As\phi_3$ molecule could not be replaced using excess of HTBA and increasing reaction time.

All isolated solid products were stable solid, diamagnetic and non-conducting in DMF and elemental analysis is consistent with proposed molecular formula (Table-1).

$$M^0(E\phi_3)_4 + 2HTBA \xrightarrow[\text{reflux}]{C_6H_6} [M^0(E\phi_3)_2(HTBA)_2] + 2E\phi_3$$

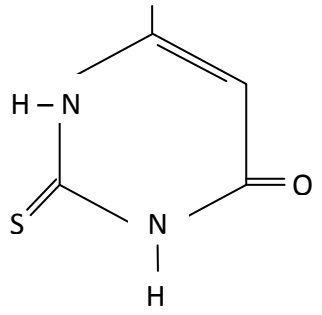
(E = P/As; M = Pd/Pt)
Scheme-1

$$[M^I(CO)(P\phi_3)_2Cl] \xrightarrow[\text{reflux}]{C_6H_6} [M(CO)(P\phi_3)(HTBA)Cl] + P\phi_3$$

(M = Rh/Ir)
Scheme-2

Spectral Characterization

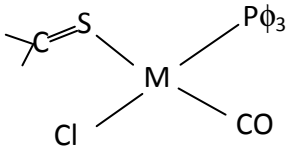
The purity of 2-thiobarbituric acid was checked from ^{1}H NMR and IR spectra. A broad peak was observed at δ4.9 PPM assigned to C_5 proton of the pyrimidine ring and sharp signal at δ12.23 PPM with integration corresponds to two NH and one OH protons as a result of $C_5 - C_6$ enolization. The appearance of νOH (2900-2910 cm^{-1}), νNH (3100, 3220 cm^{-1}), νC=O (1720 cm^{-1}), and characteristic thioamide bands between 1560-830 cm^{-1} is strong evidence for the existence of thiobarbituric acid in the following structure.



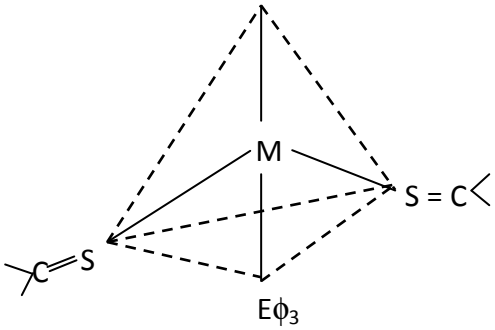
(Str.-I: HTBA)
Fig.-1

IR Spectra and mode of bonding

The presence of sharp but weak band at 2550 cm^{-1} (νSH) in free HTBA was not observed on complexation indicating thione tautomeric form and bonding through sulphur. The bonding through sulphur is confirmed by systematic shift in position and intensity of thioamide bands of free ligand (HBTA) on complexation (Table-2) considering previous observations reported in literature[20-21].



(Str.-II)
(M = Rh/Ir)



(Str.-III)
(M = Pd/Pt; E = P/As)

Fig.-2

The appearance of weak bands in far IR spectra of complexes at 330-350 cm^{-1} provides a strong evidence for the formation of Metal-S bond[22].The non-ligand new bands around 1960 cm^{-1} in Rhodium (I) and Iridium (I) complexes are assigned to terminally coordinated carbonyl group in complexes observed at higher frequency than corresponding precursor complexes[23]. The strong vibrations near 530, 690, 750 and 1550 cm^{-1} in complexes confirmed the coordinated $P\phi_3/As\phi_3$ molecules[24].
Metal-Cl stretching mode is observed at 280 cm^{-1}, which indicates $P\phi_3/As\phi_3$ groups are trans to chlorine in square planar complexes (Str. II) Shaw and Smithies[25] have reported νIr-Cl at 276 cm^{-1} and suggested trans disposition of chlorine to $P\phi_3$ considering trans effect. Jenkins et al[26] have suggested Metal-Cl stretching mode in the range of 278-262 cm^{-1} if $P\phi_3$ is trans to chlorine.

Electronic Spectra
The diamagnetic nature of Palladium(0), Platinum(0), Rhodium(I) and Iridium(I) indicates d^{10}-configuration for Pd(0) and Pt(0) and d^8-configuration for Rh(I) and Ir(I). The oxidation state of rhodium in complexes were found by titration with Cerric ammoniumsulphate using ferrion as indicator[27] and zero valent state of Palladium and Platinum was also verified by iodometric and acidimetric titration[28]. The ligand field bands in electronic spectra of complexes are obscured due to strong reducing character of Pd^0, Pt^0, Rh^+ and Ir^+ species. A single very broad band of very high intensity in the range of 350-235 nm assigned to charge transfer band and high degree of d-p mixing occurs in complexes. In the light of previous observations, the tetrahedral structure of Pd(0) and Pt(0) compelxes[29-31] and square planar configuration for Rh(I) and Ir(I) complexes[32-34] may be suggested and complexes are probably iso-structural with their precursors.

Table-1 : Analytical and physical data of thiobarbituric acid complexes

S. No.	Compound/ (MF)	Colour/ (M. Pt. 0^oC)	Found (Calculated) %				Conductance ($\wedge^{-1}cm^2mol^{-1}$)
			C	H	N	Metal	
1.	$[Pd(P\phi_3)_2(HTBA)_2]$ ($PdC_{44}H_{38}N_4O_4P_2S_2$)	Yellow (185)	57.55 (57.47)	4.88 (4.78)	6.20 (6.09)	11.62 (11.58)	10.3
2.	$[Pd(P\phi_3)(HTBA)_3]$ ($PdC_{30}H_{27}N_6O_6PS_3$)	Golden yellow (180)	44.50 (44.96)	3.40 (3.37)	10.50 (10.94)	13.60 (13.29)	6.8
3.	$[Pd(P\phi_3)_2(HTBA)(Py)]$ ($PdC_{45}H_{39}N_3O_2P_2S$)	Pale Cream (296)	(63.26)	4.66 (4.56)	4.80 (4.92)	12.16 (12.46)	7.2 8.2
4.	$[Pd(As\phi_3)_2(HTBA)_2]$ ($PdC_{44}H_{38}N_4O_4As_2S_2$)	Yellow (178)	52.54 (52.44)	3.76 (3.77)	5.54 (5.56)	10.60 (10.56)	6.3
5.	$[Pt(P\phi_3)(HTBA)_3]$ ($PtC_{30}H_{27}N_6O_6PS_3$)	Yellow (290)	40.50 (40.40)	3.10 (3.03)	9.60 (9.44)	21.80 (21.94)	6.8
6.	$[Pt(As\phi_3)_2(HTBA)_2]$ ($PtC_{44}H_{38}N_4O_4P_2S_2$)	Light yellow (225)	48.26 (48.19)	3.56 (3.46)	5.20 (5.11)	17.86 (17.81)	8.6
7.	$[Rh(P\phi_3)_2(HTBA)Cl]$ ($RhC_{40}H_{34}N_2O_2P_2SCl$)	Yellow (140)	59.83 (59.51)	4.22 (4.21)	3.50 (3.47)	12.81 (12.75)	4.6
8.	$[Rh(CO)(P\phi_3)(HTBA)Cl]$ ($RhC_{23}H_{19}N_2O_3PSCl$)	Yellow (220)	48.32 (48.20)	3.32 (3.31)	5.01 (4.89)	18.00 (17.97)	4.8
9.	$[Ir(CO)(P\phi_3)(HTBA)Cl]$ ($IrC_{23}H_{19}N_2O_3PSCl$)	Light pink (222)	41.81 (41.70)	3.50 (3.47)	4.58 (4.23)	29.00 (29.03)	6.2

^{1}H NMR Spectra
Supplementary data have been obtained by ^{1}H NMR spectroscopy recorded for the ligand (HTBA) and complexes to substantiate further metal-ligand bonding and proton chemical shift are given in table 3. The free HTBA ligand shows a resonance signal at δ12.1 PPM (S, H-N), δ4.9 PPM (S, H-C) and δ3.5 PPM

(S, H-C) which are shifted at δ11.9 – 11.6 PPM (S, H-N) and at δ4.2 – 4.3 PPM (S, H-C) on complexation. The signal at δ3.5 PPM (S, H-C) could not be observed in the ^{1}H NMR of complexes indicating enol-keto tautomerism is not established in coordinated HTBA. The iminoproton (N-H) is also intact and deprotonation of N-H may be ruled out. A broad multiplet in the range of δ7.50 – 7.80 PPM were assigned to coordinated $P\phi_3$ or $As\phi_3$ molecules[35].

Table-2 : Characterization infra red bands of ligand (HTBA) and complexes

Compounds	ν_{NH}	$\nu_{C=O}$	Thioamide Bands$^{\psi}$				ν_{M-S}	ν_{M-P}
			Band I	Band II	Band III	Band IV		
HTBA (ligand)	3100 m 3220 m	1720 (s)	1560 (s)	1300 (s)	950 m	830 m	-	-
$[Pd(P\phi_3)_2(HTBA)_2]$	3115 m 3225 m	1725 (s)	1555 (sb)	1290 (s) 1270 (s) 1240 (s)	930 m	800 m	330 w 320 w	470 m 450 m 420 m
$[Pd(P\phi_3)(HTBA)_3]$	3120 m 3230 m	1720 (sb)	1550 (sb)	1295 (s) 1280 (s)	935 m	802 m	335 w	480 m
$[Pd(P\phi_3)_2(HTBA)(Py)]$	3130 m 3235 m	1722 (sb)	1550 (sb)	1290 m 1295 m 1280 m	932 m	800 m		475 m
$[Pd(As\phi_3)_2(HTBA)_2]$	3120 m 3230 m	1725 (sb)	1555 (s)	1295 (s) 1285 (s) 1245 (s)	935 (m)	802 (m)	335 w 320 w	470 m 445 m 425 m
$[Pt(P\phi_3)(HTBA)_3]$	3115 m 3225 m	1720 (mb)	1565 (m)	1290 m 1280 m 1275 m	930 (m)	800 (m)	340 (w)	460 m
$[Pt(As\phi_3)_2(HTBA)_2]$	3150 m 3245 m	1730 (sb)	1550 (s)	1290 s 1280 s 1250 s	930 m	800 (m)	340 w	440 m 460 m
$[Rh(P\phi_3)_2(HTBA)Cl]$	3120 m 3225 m	1720 (sb)	1555 (s)	1290 s 1265 m	932 m	802 (m)	350 w	480 m
$[Rh(P\phi_3)(CO)(HTBA)Cl]$	3110 m 3230 m	1725 (sb)	1555 (s)	1310 (m)	930 (m)	805 (m)	345 w	470 (m)
$[Ir(P\phi_3)(CO)(HTBA)Cl]$	3115 m 3225 m	1730 (sb)	1560 (s)	1295 (s)	932 (m)	805 (m)	335 (w)	465 (m)

ψ : Mixed bands : Band I = δNH + δCH + δC=C; Band II = νC-N + δNH + δCH + νCS; Band III = νC – N + νC – S; Band IV = νC – S ;

Table-3 : ^{1}H NMR and electronic spectral data of ligands and complexes

	^{1}H NMR (δPPM)						
	N – H protons	CH_2 protons	Pyridine protons			$P\phi_3/As\phi_3$ protons	Electronic spectra λ (cm^{-1})
			α	β	γ		
HTBA (ligand)	12.1	4.9 3.5	—	—	—	—	287 (n→π*) 237 (π→π*)
$[Pd(P\phi_3)_2(HTBA)_2]$	11.9	4.2 —	—	—	—	7.60	315 bh (MLCT)
$[Pd(P\phi_3)(HTBA)_3]$	11.9	4.2 —	—	—	—	7.80	340 (MLCT)
$[Pd(P\phi_3)_2(HTBA)(Py)]$	11.9	4.2 —	7.65	8.22	8.88	7.78	342 (MLCT)
$[Pd(As\phi_3)_2(HTBA)_2]$	11.8	4.2	—	—	—	7.52	350 (MLCT)

		—					
$[Pt(P\phi_3)(HTBA)_3]$	11.8	4.2 —	—	—	—	7.88	345 (MLCT)
$[Pt(As\phi_3)_2(HTBA)_2]$	11.6	4.3 —	—	—	—	7.29	342 (MLCT)
$[Rh(P\phi_3)_2(HTBA)Cl]$	11.8	4.3 —	—	—	—	7.50	235 (MLCT)
$[Rh(P\phi_3)(CO)(HTBA)Cl]$	11.9	4.2 —	—	—	—	7.55	240 – 230 (CT Band)
$[Ir(P\phi_3)(CO)(HTBA)Cl]$	11.9	4.2 —	—	—	—	7.68	245 – 235 (sb) (CT Band)

Biological Studies

All the synthesized compounds were tested against gram positive bacteria S.aureus and gram negative bacteria E.coli using paper disc method reported in literature[36]. The standard drug streptomycin was used for comparison and concentration of test drug was kept 200 µg/mL in DMF. Muller Hinton Agar was used to culture the test bacteria. The microbial culture were grown at 37^0C for 8 hrs and then appropriately diluted with sterile 0.8% saline solution.

The results (Table-4) showed that the complexes exhibit moderate activity and rhodium(I) and iridium(I) complexes having coordinated chlorido group display maximum activity. The activity increases on complexation as well as increasing concentration[37-39].

Table-4 : The zone of inhibition of the compounds as well as standard drug tested for anti-bacterial activity

Compounds	Zone of inhibition (mm)			
	E.coli		S.aureus	
	200	100	200	100
HTBA	18.6	11.5	16	10.5
$[Pd(P\phi_3)(HTBA)_2]$	22.6	15.2	24.2	14.5
$[Pd(As\phi_3)_2(HTBA)_2]$	23.2	15.6	24.0	14.0
$[Pt(P\phi_3)(HTBA)_3]$	20.8	12.5	NT	NT
$[Pt(As\phi_3)_2(HTBA)_2]$	23	15	22	13
$[Rh(CO)(P\phi_3)(HTBA)Cl]$	24	16	23	15
$[Ir(CO)(P\phi_3)(HTBA)Cl]$	24	15.8	22	14
Streptomycin (Standard drug)	26.2		26.4	

Solutions = µg/mL ; NT = not tested : Temp. = 37^0C

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