Synthesis of A Novel Metal-Complex and its Polyoxometalate Based Hybrid by Solvothermal Method: Characterization and Study of their Catalytic Activity

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Abstract

A novel ruthenium metalated complex has been synthesized by co-ordinating bipyridyl molecules and 4-aryl substituted thiosemicarbazide N-(4-nitrophenyl)hydrazinecarbothioamide ligand to ruthenium(II) metal center. Phosphotungstic acid ($H_3PW_{12}O_{40}$) *was used to immobilize the ruthenium complex* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ *by solvothermal method, thus producing an organic-inorganic hybrid. The* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ *and organic-inorganic hybrid* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40}]$ *were characterized by elemental analysis, FT-IR, powder-XRD and DRUV-Vis. The change in surface morphology after the formation of hybrid from metal complex was investigated by SEM images. EDX analysis of hybrid* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40}]$ *has shown that the monomeric unit of* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ *has combined with* $[H_3PW_{12}O_{40}]$ *Keggin unit. Molecular formula of the hybrid was auxiliary confirmed by Inductively Coupled Plasma (ICP) technique. Both the metal complex and the hybrid are studied for oxidative catalytic conversion of alkyl aromatic and cycloalcohols.* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40}]$ *has exhibited better catalytic activity in terms of selectivity and conversion percentage as compared to* $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$. $Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40}]$ *was reused multiple times. The products formed during catalysis were identified by mass spectroscopy and gas chromatography..*

1. INTRODUCTION

Various ruthenium metalated complexes have been reported as homogeneous catalyst due to their photochemical, photocatalytic properties [1-6] and also for oxidation of the variety of organic substrates [7]. Ruthenium complexes exhibit eclectic range of oxidation state extending from 2+ to 6+ and also form stable ruthenium oxo species. Hence, ruthenium complexes possess exceptional catalytic activity for oxidation of organic compounds with di-oxygen species. The major drawback with homogeneous catalysts is their separation and recovery from catalytic reaction. To overcome this drawback the homogeneous catalysts must be anchored or immobilized on inorganic solid supports [8-10]. Polyoxometalates as anionic early transition metal oxide clusters can be used as solid support because they bear various properties which have significant applications in catalysis, biology and medicine [11,12]. Various hybrids that have been synthesized by immobilizing metal complexes on polyoxometalates, shown enhanced catalytic activity as compared to the respective metal complexes [13-15].

In the present research work our target is to incorporate ruthenium complex into phosphotungstic acid ($H_3PW_{12}O_{40}$), thus synthesizing new organic-inorganic hybrid $[Ru(bpy)_2\ (4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40}]$. Then both ruthenium complex and organic-inorganic hybrid will be investigated for their catalytic activity in the oxidation of cycloalcohols and 1,2,3,4-tetrahydro-naphthalene (tetralin) using tertiary butyl hydroperoxide (t-BuOOH) oxidant.

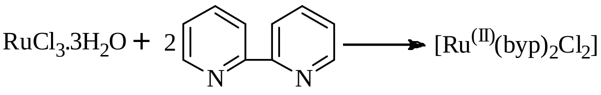
The organic-inorganic hybrid as heterogeneous catalyst has shown higher percentage of selectivity as compared to metal complex as homogeneous catalyst and was used multiple times for oxidation of substrates. The heterogeneous catalytic system allows easy product and catalyst separation. The catalytic reactions were monitored by gas chromatography (GC) and the products were further analysed by mass spectroscopy (MS) and GC. The products obtained by catalysis of the substrates are valuable intermediates and used in the manufacturing of final products in dyei, agrochemical, pharmaceutical and medicinal industries [16,17].

2. EXPERIMENTAL

Ruthenium trichloride anhydrous, 4-Nitrophenyl isothiocyanate, hydrazine hydrate and phosphotungstic acid (AR Grade) were purchased from Sigma Aldrich. 2,2-bipyridine (AR Grade) was purchased from CDH. All reagents were of analytical grade and were used without further purification. IR spectra were recorded in KBr pellets with a Nicolet170 SXFT-IR spectrophotometer in the 4000–450 cm^{-1} region. Nova Nano FE-SEM 450 (FEI) is coupled to EDAX detector for measuring the elemental composition of materials. Room temperature magnetic data were recorded for polycrystalline samples using a PPMS Versa Lab cryostat. Diamagnetic corrections were made using Pascal's constants. Thermo Scientific TSQ 8000 gas chromatograph-mass spectrometer was used for product analysis.

2.1. Synthesis of $[Ru(bpy)_2Cl_2]$

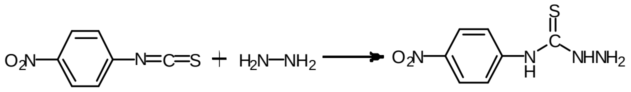
Ruthenium(II) bipyridyl complex $[Ru(bpy)_2Cl_2]$ was prepared according to thereported procedure as mentioned in reference [18]. Scheme – 1 shows synthesis of $[Ru(bpy)_2Cl_2]$. $RuCl_{3.}3H_2O$ (5 mmol) was dissolved in 10ml of dimethylformamide (DMF), then lithium chloride (33.85 mmol) and 2,2'-bipyridine (11.56 mmol) were added and the solution was kept under inert atmosphere of nitrogen for 5 minutes. The solution was stirred and refluxed for 6 hours. After 6 hours the heating was discontinued and acetonitrile (45 ml) was added to this hot solution. Then the resultant solution was stirred at room temperature for another half an hour. Then the solution was filtered yielding dark violet-black crystalline solids, which were washed with 5ml of cold D.D. water. $[Ru(bpy)_2Cl_2]$ ($RuC_{10}H_8Cl_2N_2$) (Mol. Wt. 156.18), C, 49.60; H, 3.33; N, 11.57; Found(%) C, 49.60; H, 3.30; N,11.57.



Scheme -1: Synthesis of [Ru(bpy)2Cl2]

2.2.Synthesis of N-(4-nitrophenyl) hydrazine carbothioamide

N-nitrophenyl)hydrazinecarbothioamide $[4\text{-}(p\text{-}NO_2)C_6H_4TA]$ was synthesized by dissolving 10 mmol (1.801 gm) of 4-Nitrophenyl isothiocyanate in acetonitrile then 1 mmol (0.500 ml) hydrazine hydrate was added drop-wise with continuous stirring under dry nitrogen atmosphere. Scheme - 2 shows the formation of $[4\text{-}(p\text{-}NO_2)C_6H_4TA]$. The product thus obtained was washed with acetonitrile and vacuum dried at 70°C. [4-(p-NO_2)C_6H_4TA] ($C_7H_8N_4O_2S$) (Mol. Wt. 212.23), C, 39.60; H, 3.81;N, 26.39; O, 15.08; Found (%) C, 39.61; H, 3.80; N, 26.41; O, 15.09. FT-IR (KBr) (cm^{-1}) 760, 1468, 1535, 1581, 1634 (Fig. 2a). ^{1}H NMR (200 MHz, DMSO-d_6, TMS) δ / ppm: 9.59 (s, 1H), 8.17 (d, 2H), 7.84 (d, 2H), 3.34 (s, 2H) (Fig.1).



Scheme - 2: Synthesis of N-(4-nitrophenyl) hydrazinecarbothioamide

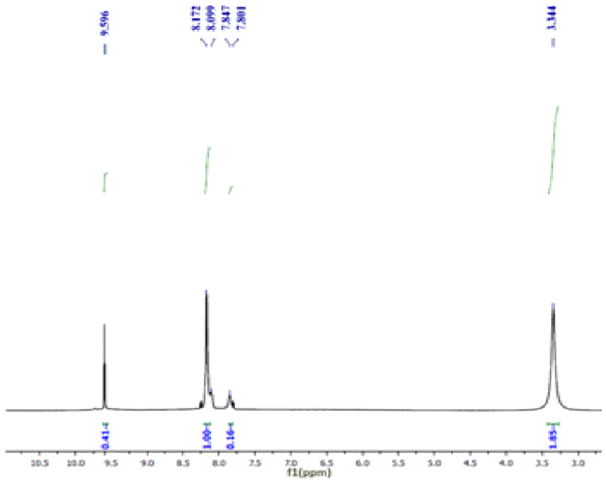
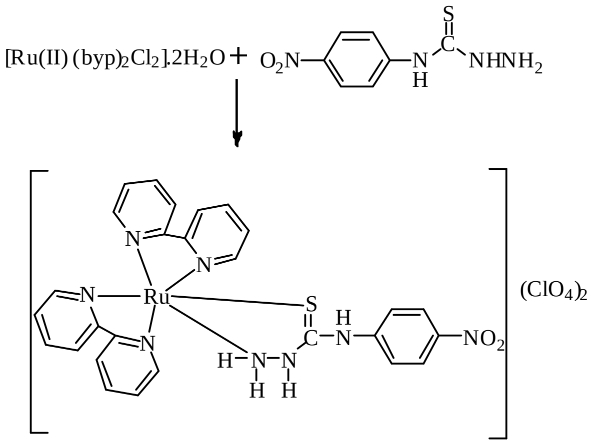


Fig.1: ^{1}H NMR of [4-(p-NO_2)C_6H_4TA] (200 MHz, DMSO-d_6, TMS)

2.3. Synthesis of [Ru(bpy)$_2$(4-(p-NO_2) C_6H_4TA)] (ClO_4)$_2$

Scheme - 3 shows the synthesis procedure of ruthenium complex, in which absolute methanolic solution of [Ru(bpy)$_2$$Cl_2$](0.5 mmol, 0.260 gm), [4-(p-NO_2)C_6H_4TA] (0.5 mmol, 0.1061 gm) was added. The resultant solution was refluxed under the dry nitrogen atmosphere at 75°C temperature for 6 hours. After reflux, the resultant solution was filtered and the volume of the filtrate was reduced to nearly half by rota-evaporator. Excess of lithium perchlorate ($LiClO_4$)was added to the solution and the solution was kept in the refrigerator. The brownish black colored precipitate that settled down was filtered and washed with D.D. water and recrystallized from dichloromethane (DCM).($RuC_{27}H_{24}N_8O_2S$) (Mol. Wt. 824.57), C, 39.4; H, 2.9; N, 13.6; O, 19.40; S, 3.81; Cl, 8.55. Found(%) C, 39.5; H, 2.9; N, 13.7; O, 19.38; S, 3.80; Cl, 8.58. FT-IR (KBr) (cm^{-1}): 650, 760, 1102, 1468, 1552, 1600, 1639.

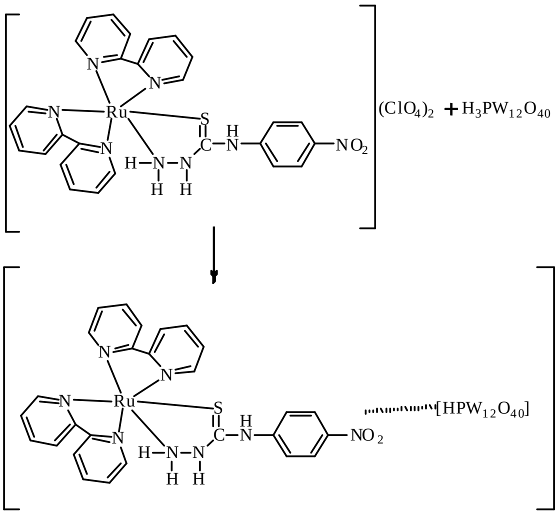


Scheme - 3: Synthesis of [Ru(bpy)2 (4-(p-NO2)C6H4TA)](ClO4)2

2.4. Synthesis of [Ru(bpy)$_2$(4-(p-NO_2) C_6H_4TA)] [$HPW_{12}O_{40}$)]

Phosphotungstic acid ($H_3PW_{12}O_{40}$) (2 mmole, 5.7601 gm) was added with constant stirring, to absolute alcoholic solution of [Ru(bpy)$_2$ (4-(p-NO_2)C_6H_4TA)] (ClO_4)$_2$(1.8770 gm, 3 mmole). The solution mixture was constantly stirred for 1 hour and then transferred to a sealed teflon reactor and heated at 110°C for 24 hours at autogenous pressure. After 24 hours of constant heating the teflon reactor was cooled down to room temperature. Brownish black colored product of Ru(bpy)$_2$(4-(p-NO_2)C_6H_4TA)][$HP_{12}O_{40}$]was obtained which was filtered and washed with absolute methanol and then vacuum dried (Scheme 5.4). Elemental analysis calculated for Ru(bpy)$_2$ (4-(p-NO_2)C_6H_4TA)] [$HP_{12}O_{40}$] $C_{27}H_{24}N_8O_{42}$ $SPRuW_{12}$(%) (Mol. wt. 3502.70) C, 9.26; H, 0.69;

N, 3.20; O, 19.18; S, 0.92; Found (%) C, 9.29; H, 0.70; N, 3.15; S, 0.96. IR spectra (KBr, cm^{-1}): 538, 750, 890, 948, 970, 1468, 1532, 1605, 1635.



Scheme –4: Synthesis of [Ru(bpy)$_2$(4-(p-NO$_2$)C$_6$H$_4$TA)][HPW$_{12}$O$_{40}$)]

3. RESULT AND DISCUSSION

Figure 2(a), 2(b) and 2(c) represent the FT-IR spectra (cm^{-1}) of [4-(p-NO$_2$)C$_6$H$_4$T A], [Ru(bpy)$_2$(4-(p-NO$_2$)C$_6$H$_4$TA)] (ClO$_4$)$_2$ and [Ru(bpy)$_2$(4-(p-NO$_2$)C$_6$H$_4$TA)] [HPW$_{12}$O$_{40}$)] respectively. The FT-IR spectra of [Ru(bpy)$_2$(4-(p-NO$_2$) C$_6$H$_4$TA)] (ClO$_4$)$_2$ (Fig.2b) shows the presence of four peaks at 1415, 1470, 1552, 1609 which are attributed to characteristic vibrations of 2,2-bipyridine. The band at 758 is due to the C=S bond vibration and the strong broad band at 1102 shows the presence of perchlorate which is not co-ordinated to Ru(II) center [19]. The bands at lower wave number 435, 500 may be assign to the vibrations ‹(Ru-N) and ‹(Ru-S) respectively [19]. The band at 1643 is due to asymmetric stretching of NO$_2$ (N=O) attached to aromatic ring in [Ru(bpy)$_2$(4-(p-NO$_2$) C$_6$H$_4$TA)] (ClO$_4$)$_2$.

The IR spectrum for the Keggin structure of [H$_3$PW$_{12}$O$_{40}$] exhibits the characteristic frequencies in the range 1,100-600 cm^{-1}. The presence of 890(s) W-O$_b$-W, 980(s) W-O$_d$, 991(sh) W-O$_d$, 1080(s) P-O, bands [20]in hybrid along with the IR bands mentioned in the metal complex with minute shifts indicate the positive interaction between cationic [Ru(bpy)$_2$(4-(p-NO$_2$)C$_6$H$_4$TA)]$^{2+}$ and anionic [HPW$_{12}$O$_{40}$]$^{2-}$.

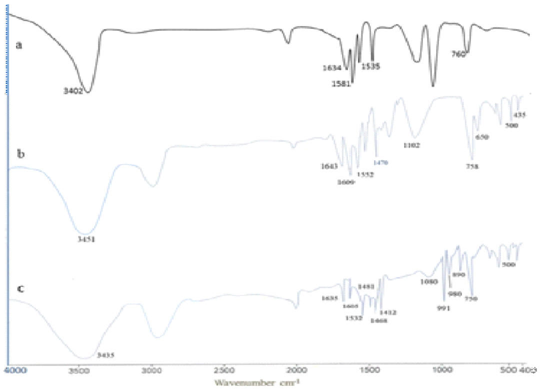


Fig.2: FT-IR (a) [4-(p-NO$_2$)C$_6$H$_4$TA] (b)[Ru(bpy)$_2$(4-(p-NO$_2$)C$_6$H$_4$TA)](ClO$_4$) (c)Ru(bpy)$_2$(4-(p-NO$_2$)C$_6$H$_4$TA)][HPW$_{12}$O$_{40}$)]

The characteristic peaks that were present in powder XRD of [Ru(bpy)$_2$ (4-(p-NO$_2$) C$_6$H$_4$TA)] (ClO$_4$)$_2$ (Fig.3a) and [H$_3$PW$_{12}$O$_{40}$] (Fig.3b) were found in [Ru(bpy)$_2$(4-(p-NO$_2$) C$_6$H$_4$TA)] [HPW$_{12}$O$_{40}$)] (Fig.3c) with minute shift. The presence of a peak around 2θ = 9 in [H$_3$PW$_{12}$O$_{40}$] and hybrid shows preservation of Keggin structure in the organic-inorganic hybrids [21]. Thus powder-XRD indicates the incorporation of metal complex into phosphotungstic acid.

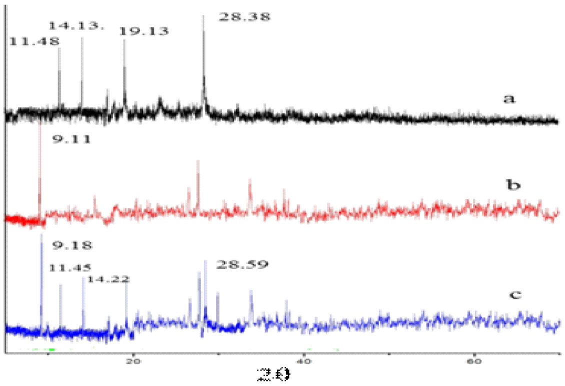


Fig.3 : Powder XRD (a)[Ru(bpy)$_2$ (4-(p-NO$_2$)C$_6$H$_4$TA)] (ClO$_4$)$_2$ (b) H$_3$PW$_{12}$O$_{40}$ (c) [Ru(bpy)$_2$(4-(p-NO$_2$) C$_6$H$_4$TA)][HPW$_{12}$O$_{40}$)]

Drastic change shown by SEM images in surface morphology of the newly synthesized hybrid as compared to metal complex indicates the immobilization of $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ onto the surface of $H_3PW_{12}O_{40}$. Figure 4(a) and 4(b) shows SEM micrographs of $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ and $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][(HPW_{12}O_{40})]$.

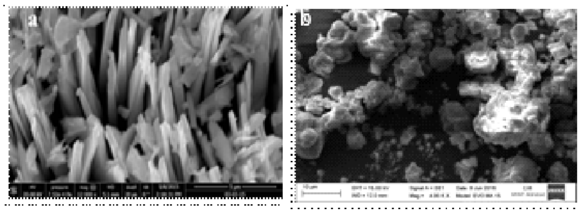
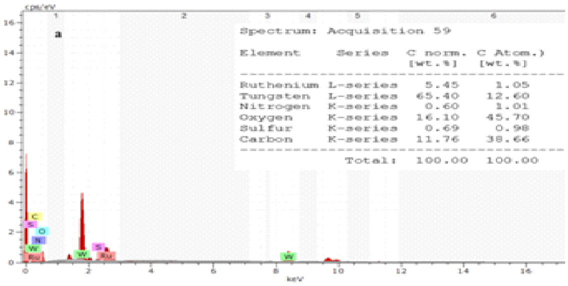


Fig.4: SEM Image (a) $[Ru(bpy)_2\ (4\text{-}(p\ NO_2)\ C_6H_4TA)](ClO_4)_2$ (b)$[Ru(bpy)_2\ (4\text{-}(p\text{-}NO_2)C_6H_4TA)]\ (HPW_{12}O_{40})]$

EDX analysis of the hybrid reveals the presence of all the expected elements. The EDX analysis which was performed in the SEM chamber confirmed the stoichiometry of $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][(HPW_{12}O_{40})]$ (Fig.5) was 1 Ru atom per Keggin unit. The ICP-OES analysis of Ru, W in the hybrid further corroborated that $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][(HPW_{12}O_{40})]$ have $C_{27}H_{24}N_8O_{42}SPRuW_{12}$ formula (Table 1). The ICP-OES data for W and Ru in $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40})]$ are close to the values calculated for the suggested chemical formula which indicates that the cationic $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]^{2+}$ immobilized on anionic Keggin structure $[HPW_{12}O_{40}]^{2-}$. Calculated for$[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][(HPW_{12}O_{40})]$%: W 63.71.1, Ru 2.95; found (%): W 63.86, Ru 2.98.



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Spectrum: Acquisition 59

Element     Series    C norm.  C Atom.)
                      [wt.%]   [wt.%]
-----------------------------------------
Ruthenium  L-series    5.45     1.05
Tungsten   L-series   65.40    12.60
Nitrogen   K-series    0.60     1.01
Oxygen     K-series   16.10    45.70
Sulfur     K-series    0.69     0.98
Carbon     K-series   11.76    38.66
-----------------------------------------
               Total: 100.00   100.00
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Fig. 5: EDX $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][(HPW_{12}O_{40})]$

Table-1: ICP of $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)\ C_6H_4TA)][HPW_{12}O_{40})]$

Element	Concentration	Wavelength
Ruthenium(Ru)	0.005 gm/L	243.198 nm
Tungsten(W)	0.129 gm/L	241.689 nm

In DR UV-Vis spectra (Fig.6a) of $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ the band at 676 nm in the metal complex is due to the metal-to-ligand charge transfer (MLCT) between t_2g orbital of ruthenium (Ru^{2+}) and a π^* orbital of thiosemicarbazide ligand, this band also confirmed the presence of ruthenium in dicationic form since the band around 600-700 nm is a characteristic of all dicationic species [22]. A band around 290 nm was observed which is the characteristic band due to π-π^* electronic transition of bipyridine ligand, however this band was overlapped with the ligand-to-metal charge-transfer (LMCT) band for the tungsten (O→W) in the DR UV-Vis of hybrid $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40})]$. Figure 6(b) shows the DR UV-Vis of the Keggin type $H_3W_{12}O_{40}$. The DR UV-Vis spectra of the hybrid shows hypsochromic shift as compared to the $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]\ (ClO_4)_2$ spectra. The characteristic peaks of $[H_3PW_{12}O_{40}]$ and $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ are present in the hybrid $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40})]$ (Fig.6c) which shows that cationic ruthenium complex $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]^{2+}$ is immobilized by polyanion $[HPW_{12}O_{40}]^{2-}$.

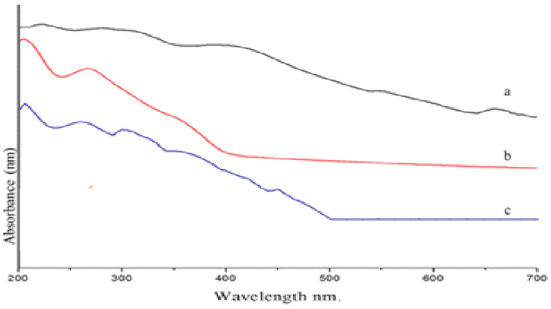


Fig.6: DR UV-Vis (a) $[Ru(bpy)_2\ (4\text{-}(p\text{-}NO_2)\ C_6H_4TA)](ClO_4)_2$ (b) $[H_3PW_{12}O_{40}]$ (c)$[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]\ [(HPW_{12}O_{40})]$

4. CATALYTIC EVALUATION

The oxidative catalytic activity of novel $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40})]$and $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ was investigated. Tetralin, cyclohexanol and cyclopentanol as substrates were successfully oxidized by ruthenium complex and the hybrid as catalyst into useful industrial and pharmaceutical products. In order to optimize catalytic reaction condition various solvents were tested using tetralin as reference substrate. Maximum product yield was obtained with acetonitrile solvent as compared with glacial acetic acid, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) solvent. In addition, temperature was optimized by performing the catalytic reaction at different temperature keeping the other parameters constant. Maximum yield for tetralin was obtained at 70°C (±1°C).

For catalytic evaluation experiments 0.01 mmol of hybrids, 1 ml of substrate, 5 ml of acetonitrile (CH_3CN) solvent and 0.5 ml of tertiary butyl hydroperoxide (t-BuOOH) as oxidant were taken in 25 ml volume round bottom (RB) vessel. The reaction mixture was refluxed at 70ÚC (±1ÚC) temperature and monitored by GC. The progress of the reaction was monitored after each hour. The catalytic experiments were carried for different time intervals (3 hours - 8 hours) depending upon the maximum product yield.

Blank catalytic experiments without catalyst were also performed using same reaction condition, no measurable product yield was found. The catalytic experiment using $[H_3PW_{12}O_{40}]$ was also performed under similar condition but no measurable yield were obtained. After the first run of catalytic experiment, the hybrid catalyst was reused after washing with D.D. water, methanol, diethyl ether. The percent conversion of substrates as well as percent selectivity to their respective products during first run by the catalyst is represented in Table 2. Percent conversion of tetralin, cyclohexanol and cyclopentanol during first and second run is graphically shown in bar-graph-1. DRS UV-Vis spectra of the hybrid (Fig. 7) taken after first catalytic run shows absorbance at similar wavelength (nm) as given in figure 6c. The catalytic activity unfortunately, reduced slightly after first run and no catalytic activity was observed during third catalytic run.

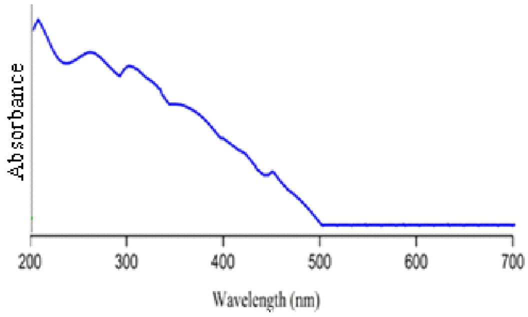
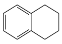
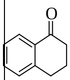
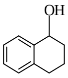
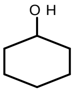
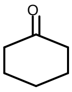
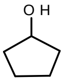
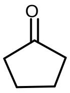
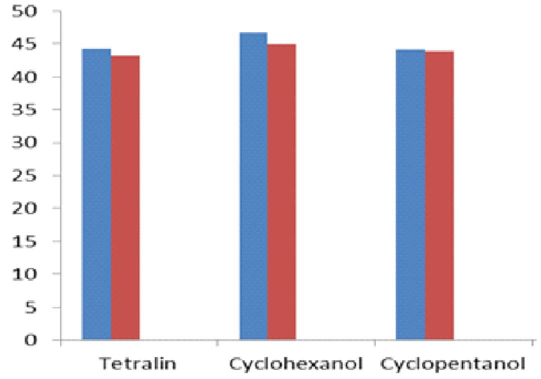


Fig.7: DR-UV-Vis after 1^{ST}catalytic run $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]\ [(HPW_{12}O_{40})]$

Table -2 :
(i) %Coversion and Selectivity shown by $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)](ClO_4)_2$ as catalyst
(ii)%Coversion and Selectivity shown by $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)(HPW_{12}O_{40})]$ as catalyst

S.No	Substrate	Product	Conversion %	Selectivity %	Time (hr)
1	 Tetralin	(A) (B)   1-Tetralone 1-Tetralol	41.84 (i) 47.64 (ii)	(A) (B) 75.41 24.59 (i) 82.48 17.52 (ii)	3 (i) 2(ii)
2	 Cyclohexanol	 Cyclohexanone	40.54 (i) 48.88 (ii)	100(i) 100(ii)	3(i) 2(ii)
3	 Cyclopentanol	 Cyclopentanone	40.07 (i) 45.97 (ii)	100(i) 100(ii)	4(i) 3(ii)



Bar Graph-1:$[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)][HPW_{12}O_{40}]$ as catalyst

🟦 % Conversion of Tetralin during first run
🟥 % Conversion of Tetralin during second run
🟦 % Conversion of Cyclohexanol during first run
🟥 % Conversion of Cyclohexanol during second run
🟦 % Conversion of Cyclopentanol during first run
🟥 % Conversion of Cyclopentanol during second run

5. CONCLUSION

A novel metal complex comprising of 2,2'-bipyridine, N-(4-nitrophenyl) hydrazine carbothioamide ligand coordinated to ruthenium metal center was synthesized. Then the metal complex $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]\ (ClO_4)_2$ was immobilized by phosphotungstic acid, to synthesize a new organic–inorganic POM based hybrid $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]\ [HPW_{12}O_{40})]$. The hybrid was synthesized by solvothermal method by interaction between cationic $[Ru(bpy)_2(4\text{-}(p\text{-}NO_2)C_6H_4TA)]^{2+}$ and anionic $[HPMo_{12}O_{40}]^{2-}$. Characterization by various techniques confirmed that the hybrid has chemical formula $C_{27}H_{24}N_8O_{42}SPRuW_{12}$. The hybrid shown higher percent of conversion and selectivity as compared to the metal complex. The catalytic activity of hybrid was reused during second run and finally no catalytic activity was found during third run. The products obtained during catalysis are used as valuable reaction intermediate for the formation of final products in dyes, pharmaceutical and polymer industries.

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