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Preparation and characterization of new chitosan 2,4-dihydroxybenzaldehyde Schiff-base complexes; catalytic epoxidation of 1-hexene in presence of H_2O_2

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ABSTRACT

The chitosan 2,4-dihydroxybenzaldehyde Schiff-base (H_2cs-ba) was prepared by the condensation of 2,4-dihydroxybenzaldehyde and chitosan (cs) in ethanol. The Schiff-base complexes of Fe(III), Co(II), Ni(II), Ru(III), Rh(III) and Pd(II) were reported. They were characterized by spectroscopic (IR, ^{13}C NMR, UV-VIS, SEM and XRD), elemental analysis, magnetic and thermal measurements. The Schiff-base (H_2cs-ba) behaves as mononegative bidentate and coordinates the metal ions *via* the azomethine nitrogen and deprotonated 2-hydroxy groups. The catalytic oxidation of 1-hexene to epoxyhexane by some of the reported complexes was also reported.

KEYWORDS

Schiff-base;
Chitosan;
H_2cs-ba;
1-Hexene;
Epoxidation.

INTRODUCTION

Chitosan (cs), is a β-(1→4) linked biopolymer of 2-amino-2-deoxy-D-glucose repeating units[1-3]. Chitosan is the most abundant free amino polysaccharide naturally occurs and it has wide range of applications ranging from adsorption of metals, waste water treatment, photography, food and nutrition, cosmetic and artificial skin[4]. The free amino groups of chitosan enable a variety of chemical modifications in the polymeric chain including Schiff's-bases and metal chelation[5]. The Schiff-base modified derivatives offered good catalysts for cyclopropanation, olefin oxidation and C-C coupling reactions[6-8].

We have early reported the chemistry of Schiff-base derived from salicylaldehyde and 3-aminopropyltriethoxysaline complexes anchored in NaY-zeolite and their applications in catalytic epoxidation of olefins[9]. Also, we have recently reported the preparation, characterization and pH-metric measurements of transition metal complexes of 4-hydroxysalicylidene-2-amino pyrimidine Schiff-base[10,11].

The reactions of chitosan with variety of aromatic aldehydes in acetic acid to produce the corresponding Schiff-bases have been reported[3,5,12-15]. The modification in the amino function group (NH_2) in the chitosan matrix may improve its capacity of interaction with transition metal ions through complex formation[16]. The degree of substitution of chitosan through Schiff-base formation is depending on the stoichiometric amount of aldehyde and the conditions applied in the reaction[17].

Herein we have synthesized a Schiff-base derived from chitosan and 2,4-dihydroxybenzaldehyde (H_2cs-ba) and its metal-polymer complexes; [M(Hcs-ba)$Cl_2(H_2O)_2$] (M(III) = Fe, Ru, Rh), [M'(Hcs-ba)(AcO)$(H_2O)_2$] (M'(II) = Co, Ni) and [Pd(Hcs-ba)Cl(H_2O)]. They have been characterized on the bases of elemental analyses, spectral (IR, solid ^{13}C NMR, electronic, SEM and XRD), magnetic and thermal measurements. In addition, we report the catalytic epoxidation of 1-hexene in presence of H_2O_2.

EXPERIMENTAL

Preparation of chitosan 2,4-dihydroxybenzaldehyde Schiff-base (H_2cs-ba).$2H_2O$

H_2cs-ba was synthesised by the condensation of a suspension of chitosan (2.0 g, 12 mmol) and 2,4-dihydroxybenzaldehyde (1.38 g, 10 mmol) in ethanol (30 cm^3) the mixture was refluxed with stirring for 30 h. The orange product was filtered off, washed with ethanol, diethyl ether and dried in *vacuo*. *Elemental Anal.* Calc. for $C_{19}H_{30}N_2O_{12}$: C, 47.7; H, 6.3; N, 5.9%. Found C, 47.2; H, 6.4; N, 5.6 %. IR: ν(CH=N), 1630; ν(C-O), 1235 cm^{-1}. Solid^{13}C- NMR (δ, ppm): 104.85 C(1); 58.26 C(2); 75.29 C(3); 98.20 C(4); 83.11 C(5); 61.30 C(6); 174.07 H(C=N); 119.00 C($1^{\backslash}$);165.42 C($2^{\backslash}$); 103.00 C($3^{\backslash}$); 163.40 C ($4^{\backslash}$); 111.50 C($5^{\backslash}$); 134.90 C($6^{\backslash}$) ppm.

Preparation of the complexes

[Fe(Hcs-ba)$Cl_2(H_2O)_2$].$2H_2O$

To a suspension of H_2cs-ba (0.25 g, 0.75mmol) in ethanol (15 cm^3), an ethanolic solution (2 cm^3) of $FeCl_3$ (0.121 g, 0.75mmol) was added. The resulting suspension was heated under reflux for 5 h till brown precipitate was formed. It was filtered off during hot, washed with ethanol, diethylether and dried *in vacuo*. *Elemental Anal.* Calc.for $C_{19}Cl_2FeH_{33}N_2O_{14}$ C, 35.6; H, 5.2; N, 4.4; Cl, 11.1%. Found C, 35.2; H, 5.3; N, 4.2; Cl, 11.2%. IR: ν(CH=N) 1626; ν(C-O)1234; ν(Fe -O) 530; ν(Fe -N) 407; ν(Fe -Cl) 332 cm^{-1}.

[Ni(Hcs-ba)(AcO)$(H_2O)_2$].$2H_2O$

$Ni(AcO)_2.4H_2O$ (0.186 g, 0.75 mmol) in ethanol (5 cm^3) was added to a suspension of H_2cs-ba (0.25 g, 0.75 mmol) in ethanol (10 cm^3). The reaction mixture was stirred under reflux 12h. The orange precipitate obtained was filtered off during hot, washed with ethanol, diethylether and dried *in vacuo*. *Elemental Anal*. Calc. for $C_{21}H_{36}N_2$ Ni O_{16} C, 40.0; H, 5.7; N, 4.4%. Found C, 40.3; H,6.1; N, 4.8%. IR: ν(CH=N) 1625; $\nu_{as}(COO^-)$1563; $\nu_s(COO^-)$1484 ;ν(C-O)1226; ν(Ni-O) 553; ν(Ni-N) 43 cm^{-1}.

[Co(Hcs-ba)(AcO)$(H_2O)_2$].$2H_2O$

Similar procedure as the nickel analogue were applied using $Co(AcO)_2$ to produce red-brown precipitate. *Elemental Anal.* Calc. for $C_{21}CoH_{36}N_2O_{16}$ C, 40.0; H, 5.7; N, 4.4%. Found C, 40.1; H, 5.7; N, 4.4%. IR: ν(CH=N) 1625; $\nu_{as}(COO^-)$1593; $\nu_s(COO^-)$1483; ν(C-O)1228; ν(Co -O) 527; ν(Co -N) 420cm^{-1}.

[Ru(Hcs-ba)$Cl_2(H_2O)_2$].H_2O

An ethanolic solution (25 cm^3) of hydrated $RuCl_3$ (0.187 g, 0.75 mmol) was added dropwise to a suspension of H_2cs-ba (0.25 g, 0.75 mmol,) in potassium ethoxide (2 mmol of KOH in 25 cm^3 of ethanol). The resulting mixture was stirred for 30 min and then kept under reflux for 8 h. The green-brown solid obtained was filtered off during hot, washed with ethanol, diethylether and dried *in vacuo*. *Elemental Anal.* Calc. for $C_{19}Cl_2H_{31}N_2O_{13}$Ru C, 34.2; H,4.6; N, 4.2 ; Cl, 10.6%. Found C,34.0; H,4.7; N, 4.1; Cl, 10.3 %. IR: ν(C=N) 1624; ν(C-O) 1220; ν(Ru-O) 527; ν(Ru-N) 467; ν(Ru -Cl) 321 cm^{-1}.

[Pd(Hcs-ba)Cl(H_2O)].$2H_2O$

An aqueous solution of $K_2[PdCl_4]$ (0.245 g, 0.75 mmol; 2 cm^3) was added to a suspension of H_2cs-ba (0.25 g, 0.75 mmol) in ethanol (10 cm^3). The resulting suspension was heated under reflux for 5 h till a dark green precipitate was formed. It was filtered off during hot, washed with water, ethanol, diethylether and dried *in vacuo*. *Elemental Anal*. Calc. for $C_{19}ClH_{31}N_2O_{13}$Pd: C, 35.80; H, 4.9; N, 4.4; Pd, 16.7; Cl, 5.6%. Found C, 35.4; H, 4.4; N, 4.4; Pd, 16.9; Cl, 5.5 %. IR: ν(CH=N) 1627; ν(C-O) 1257; ν(Pd-O) 501; ν(Pd-N) 434; ν(Pd-Cl) 319 cm^{-1}. Solid^{13}C- NMR (δ, ppm): 104.93 C(1); 58.27, 58.32 C(2); 75.33 C(3); 98.28 C(4); 83.21 C(5); 61.34 C(6); 174.50 H(C=N); 119.11 C($1^{\backslash}$);165.51 C($2^{\backslash}$); 103.08 C($3^{\backslash}$); 163.42 C ($4^{\backslash}$); 111.53 C($5^{\backslash}$); 134.94 C($6^{\backslash}$) ppm.

$[Rh(Hcs\text{-}ba)Cl_2(H_2O)_2].2H_2O$

An aqueous solution of hydrated $RhCl_3$ (0.2 g, 0.75 mmol) was added to *H_2cs-ba* (0.25 g, 0.75 mmol). An aqueous solution of CH_3COONa (0.62 g, 7.5 mmol) in water (10 cm^3) was added. The reaction mixture was stirred and heated under reflux for 8 h. The orange precipitate was separated out, washed with hot water and air-dried. *Elemental Anal.* Calc. for $C_{19}Cl_2H_{33}N_2O_{14}Rh$ C,33.2; H,4.8; N,4.1; Cl, 10.3%. Found C,33; H,4.6; N, 4.0; Cl, 10.2%. IR: ν(CH=N) 1621; ν(C-O)1233; ν(Rh -O) 527; ν(Rh -N) 433; ν(Rh -Cl) 335 cm^{-1}. Solid^{13}C- NMR (δ, ppm): 104.89 C(1); 58.26, 58.43 C(2); 75.33 C(3); 98.27 C(4); 83.18 C(5); 61.32 C(6); 174.51 H(C=N); 119.09 C(1$'$); 165.51 C(2$'$); 103.10 C(3$'$); 163.42 C(4$'$); 111.52 C(5$'$); 134.96 C(6$'$) ppm.

Epoxidation of 1-hexene

In a typical oxidation procedure, a Pyrex tube (20 cm^3) was charged with the complex (catalyst; 0.0125 g), 1-hexene (2 cm^3) and 30% aqueous H_2O_2 (1 cm^3). The reaction mixture was heated at 353 K with stirring in paraffin-oil bath. The reaction products were determined and analyzed after 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 hours in the GC-Mass.

Materials & Instrumentations

All manipulations were performed under aerobic conditions using materials and solvents as received. Chitosan, 2,4-dihydroxybenzaldehyde were obtained from Aldrich. $FeCl_3$, $Co(CH_3COO)_2$, $Ni(CH_3COO)_2$, $RuCl_3$, $RhCl_3$ and K_2PdCl_4 were of extra pure quality and obtained from sigma-Aldrich Chemie GmbH, Germany. Ethanol, diethylether, acetonitrile, 1-hexene and dimethylformamide were obtained from E. Merk, and directly used. Chitosan (cs) with a molecular weight of 161 and 0% degree of acetylation was used. The Schiff-base 4-hydroxysalicylidene-chitosan (H_2cs-ba) have a water content of 7.5 ± 0.1 % (w/w).

Elemental analyses (C, H, N, Cl) were performed by The Micro Analytical Unit of Cairo University. Magnetic moments at 25 °C were recorded using a Johnson Matthey magnetic susceptibility balance with $Hg[Co(SCN)_4]$ as calibrant. IR spectra were measured as KBr discs on a Matson 5000 FT-IR spectrometer. Electronic spectra were recorded using a Unicam $UV_{2\text{-}100}$ U.V.-vis. Spectrometer. Thermal analysis measurements were made in the 20 – 800° C range at the heating rate of 10° C min^{-1}, using α-Al_2O_3 as a reference, on a Shimadzu Thermogravimetric Analyzer TGA-50. X-ray powder diffraction were determined using a Bruker diffractometer (Bruker D8 advance target), the scan rate was fixed at 8° in 2θ min^{-1} for phase identification. The patterns were run with $CuK\alpha_1$ with secondly monochromator (λ = 0.1545 nm) at 40 kV and 40 mA. Solid ^{13}C NMR spectra were measured on varian Mercury 400 MHz spectrometer and SEM were carried out using a Hitachi S-3000 VP_SEM Variable Pressure-SEM with an Oxford Inca EDS for the element analysis. The epoxidation reaction products were determined and analyzed by Shimadzu GC-Mass.

RESULTS AND DISCUSSION

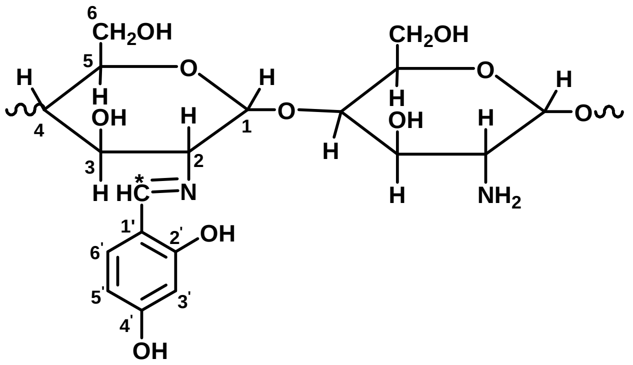
In the preparation of Schiff-base (H_2cs-ba), chitosan acts as a primary amine reacts with 2,4-dihydroxybenzaldehyde to produce the biopolymeric derivative, H_2cs-ba. The elemental analyses of the isolated Schiff-base (H_2cs-ba) and its complexes agree with the assigned formulae as shown in the experimental section. The complex $[Fe(Hcs\text{-}ba)Cl_2(H_2O)_2]$ was prepared by the reaction of H_2cs-ba with $FeCl_3$ in ethanol. $[Co(Hcs\text{-}ba)(AcO)(H_2O)_2]$was obtained by the reaction of H_2cs-ba with hydrated Co(AcO) in ethanol. The complex $[Ru(Hcs\text{-}ba)Cl_2(H_2O)_2]$ made from hydrated $RuCl_3$ with H_2cs-ba in basic ethanol. The complex $[Pd(Hcs\text{-}ba)Cl(H_2O)]$ was isolated from the reaction of K_2PdCl_4 and H_2cs-ba in aqueous-ethanolic solution. Finally, $[Rh(Hcs\text{-}ba)Cl_2(H_2O)_2]$ was obtained from the reaction of H_2cs-ba and hydrated $RhCl_3$ under aqueous basic conditions.

The complexes are stable in the normal laboratory atmosphere and partially soluble in DMF and DMSO. As the complexes are chemically anchored in chitosan, the characterization of these complexes was based on physical and spectroscopic techniques.

IR spectroscopy

The IR spectrum of the chitosan (cs) exhibits a strong broad band at 3500 cm^{-1} corresponding to ν(OH) stretch[15] while the axial stretching of C-H groups observed at 2900 cm^{-1}[9]. The bands at 3330 and 3470 cm^{-1} arise from $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ stretches, respectively[10,19].

The solid-state properties of the Schiff-base (H_2cs-ba, Structure 1) were examined by IR spectroscopy. The spectrum was compared with those of the complexes. Tentative assignments of selected IR bands are reported in the experimental section. The general features are similar to those observed for the other chitosan Schiff-bases and their complexes reported[13-15,20,21].



Structure 1: Schiff-base H_2cs-ba

In the IR spectrum of the Schiff-base (H_2cs-ba; Figure 1), no band observed in 1660 – 1730 cm^{-1} region related to the free aldehyde group or H-bonding, indicating that 2,4-dihydroxybenzaldehyde has been successfully grafted onto the chitosan backbone to obtain the Schiff-base H_2cs-ba[13]. The IR spectrum of H_2cs-ba shows absorption bands at 1630 and 1235 cm^{-1} arise from the azomethine ν(HC=N)[10,15] and ν(C-O')[10] stretches, respectively. It is expected that coordination of the nitrogen centre to the metal ion would reduce the electron density in the azomethine link and thus shifted the (HC=N) to lower wave numbers[22]. In the IR spectra of the complexes, this band is shifted to the region at 1620 – 1626 cm^{-1}[22,23]. The bands observed at 3330 and 3470 cm^{-1} arise from $\nu_s(NH_2)$ and $_{as}(NH_2)$ stretches, respectively, indicating partial condensation of the amino group through Schiff-base formation. Also, the shift of the phenolic ν(C-O') stretch indicates the coordination of H_2cs-ba through the deprotonated phenolic $(C_2\text{-}O'^{-})$[24]. In the IR spectrum of H_2cs-ba two more bands are observed at 3387 and 3217 cm^{-1} attributed to the phenolic ν(2-O'H) and ν(4-O'H) stretches, respectively[10]. In the complexes, the broad band at 3388 cm^{-1} attributed to ν(2-O'H) is disappeared; the deprotonation occurs prior to coordination, while the band at 3221 cm^{-1} due to ν(4-O'H) stretch is unaffected by coordination[25]. The spectra of the free Schiff-base (H_2cs-ba) and its complexes show bands near 2922, 2885 and 1562 cm^{-1} are attributed to $\nu_{as}(CH_2)$, $\nu_s(CH_2)$ and ν(C=C) stretches, respectively[9,20]. The first two bands are not affected while the later one is slightly shifted upon coordination. The vibrational spectral data suggest azomethine nitrogen (CH=N) and deprotonated hydroxyl $O^-(2')$ mononegative bidentate of (Hcs-ba). Structure 2 shows the structure of [M'(Hcs-ba)(AcO)$(H_2O)_2$] (M'(II) = Co, Ni). In the acetato complexes, two extra bands observed near 1535 and 1400 cm^{-1} are due to $\nu_{as}(OCO^-)$ and $\nu_s(OCO^-)$ of the acetato group, respectively indicating asymmetric bidentate coordination of the acetate group[9,26].

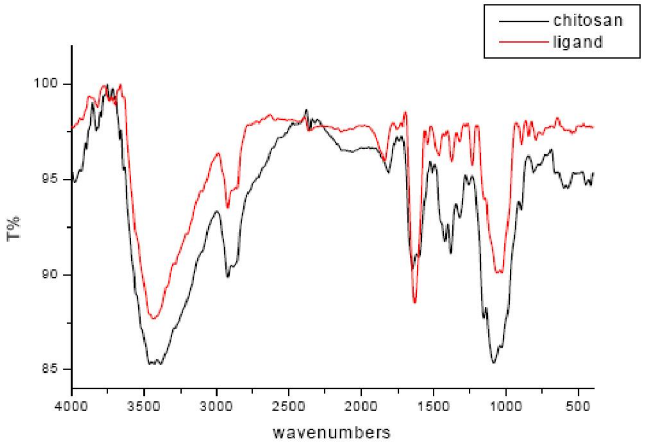
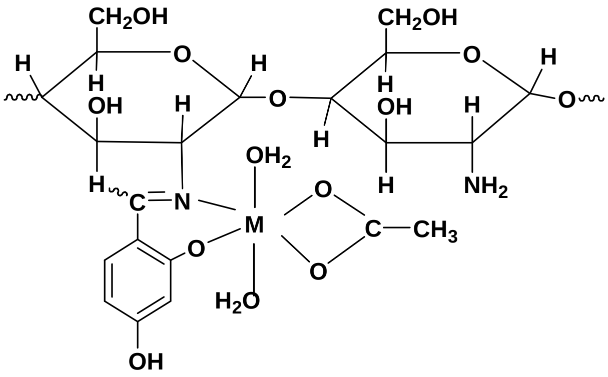


Figure 1 : IR spectra of cs and H_2cs-ba



Structure 2 : Structure of [M(Hcs-ba)(AcO)$(H_2O)_2$] (M(II) = Co, Ni)

The region of the complex spectra between 520 and 200 cm^{-1} contains several weak bands; these may assign to ν(M-O), ν(M-N) and ν(M-Cl) stretches, respectively[9,10,19].

^{13}C NMR spectra

The solid state ^{13}C NMR of of H_2cs-ba (Figure 2) and some of the representative complexes are listed in the experimental section. The ^{13}C NMR spectrum of the free H_2cs-ba exhibits bands at δ 58.26, 61.30, 75.29, 83.11, 98.20, 103.00, 104.85, 111.50, 119.00, 134.90, 163.40, 165.42, 174.07 ppm, these probably arise from C(2), C(6), C(3), C(5), C(4), C(3'), C(1), C(5'), C(1'), C(6'), C(4'), C(2'), C(CH=N), respectively (see Structure 1 for numbering scheme)[27-29]. No bands observed near δ 20.00 ppm confirming the non-acetylation of the used chitosan[5]. In the complexes, the resonances for the carbon atoms adjacent to the coordination sites, C(2), C(2') and C(CH=N), are shifted downfield relative to their positions in the free Schiff-base and appeared near δ 58.30, 165.65 and 174.50 ppm[27]. Hence, half of C(2) amino groups were undergo Schiff-base formation as a strong signal at δ 58.25 ppm is still observed[29].

Figure 2 : Solid ^{13}C NMR of H_2cs-ba

Electronic spectra

The electronic spectra of H_2cs-ba and its complexes were recorded in DMSO and Nujol in the 200 – 800 nm range. Transition below 400 nm are assigned to intra-ligand charge transfer (n→π*) and (π→π*). The electronic spectra of the complexes contain intense bands due to ligand to metal charge transfer (LMCT) and weaker bands assigned to d-d transitions[30].

The electronic spectrum of the diamagnetic [Rh(Hcs-ba)$Cl_2(H_2O)_2$] complex displays bands at 550, 504 and 423 nm which resemble those of other six-coordinate Rh(III) complexes and may assign to $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively[19,31].

The electronic spectrum of the diamagnetic [Pd(Hcs-ba)Cl(H_2O)] shows bands at 490 and 352 nm due to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions in a square planar environment around Pd(II)[31,32]

The electronic spectrum of [Ru(Hcs-ba)$Cl_2(H_2O)_2$] complex shows high intense transitions at 520 ($^2T_{2g} \rightarrow {}^2T_{2g}$, ^2E_g), 468 ($^2T_{2g} \rightarrow {}^2T_{1g}$, $^2A_{1g}$) and 338 (ligand (π-dπ)) nm. The magnetic moment of 2.1 B. M. Lies within the range reported for low-spin octahedral Ru(III) complexes[22,33]

The electronic spectrum of [Ni(Hcs-ba)(AcO)$(H_2O)_2$] can be interpreted in a terms of a distorted octahedral stereochemistry around the nickel centre. The $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition appears at 860 and 802 nm, probably caused by a distortion from regular octahedral while the strong band at 432 nm can be assigned to a combination of $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and charge transfer transitions[10]. The magnetic moment of 3.08 B. M. lies within the range reported for octahedral Ni(II) complexes[34,35].

The magnetic moment of [Fe(Hcs-ba)$Cl_2(H_2O)_2$] is 4.98 B. M. The electronic spectrum of this complex shows absorption band at 540 and 376 nm similar to $^6A_{1g} \rightarrow {}^4T_{2g}$ and charge transfer in high spin-octahedral Fe(III) complex[35,36].

The electronic spectrum of [Co(Hcs-ba)(AcO)$(H_2O)_2$] exhibits two absorption bands at 570 and 503 nm are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^1T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively. The magnetic moment recorded for this complex is 5.4 B. M., in a greet agreements with octahedral high-spin Co(II) complexes[37].

Thermal measurements

The thermal stability and degradation behaviour of the Schiff-base (H_2cs-ba.2H_2O) and its complexes, [Fe(Hcs-ba)$Cl_2(H_2O)_2$].2H_2O, [Co(Hcs-ba)(AcO)$(H_2O)_2$].2H_2O and [Pd(Hcs-ba)Cl(H_2O)].2H_2O was studied using thermo-gravimetric (TG) technique. The weight loss observed below 150 °C is due to dehydration as colours changed from pale to deep[11,25]. According to the TG curves, there are four mass loss stages arising from the lattice water elimination, coordinated water and free amino cs-unit, decomposition of condensed cs and 4-hydroxysalicylidene units, respectively.

The thermogram of H_2cs-ba.2H_2O shows the first step weight loss of 7.4% between 35 and 108 °C, which corresponds almost exactly to the release of two mol of H_2O per mol of Schiff-base (Calcd. 7.5%); the relatively low temperature of water loss shows that these water molecules are crystal lattice held[11]. Another endothermic decomposition occurs between 244 and 396 °C, this weight loss is attributed to the loss of free amino cs-unit ($C_6H_{11}NO_4$) fragment (Calcd. 33.7 Found 34.1%). There are two other TG inflections in the ranges 397 – 509 and 510 – 700 °C, may arise from the elimination of condense chitosan C_6H_9O (Calcd. 20.3, Found 20.7%) and $C_7H_6NO_2$ (Calcd. 28.5, Found 28.7%) fragments.

The thermogram of [Fe(Hcs-ba)$Cl_2(H_2O)_2$].$2H_2O$ is characterized by steps at 36 – 149, 150 – 331, 332 –530 and 533 – 783 °C regions. The elimination of crystal lattice water (Calcd. 5.6, Found 5.1%)[11], coordinated water and cs-unit ($C_6H_{11}NO_4$) (Calcd. 30.8, Found 30.9%), Cl_2 and CO_2 (Calcd. 18.0, Found 18.4%), C_7H_5NO (Calcd. 18.6, Found 19.3%) fragments, respectively, leaving mixed iron oxide and carbide residues at 800 °C (22.7%).

The thermograms of [Co(Hcs-ba)(AcO)$(H_2O)_2$].$2H_2O$ shows four TG inflections in the ranges 30 – 130, 197 – 390, 390 – 450 and 490 – 700 °C. The first weight loss arises from the elimination of crystal lattice water (Calcd. 5.7, Found 5.7%)[10]. The second step may arise from the release of coordinated water, cs-unit ($C_6H_{11}NO_4$) and acetato fragments (Calcd. 40.6, Found 39.8%)[26], the third step is due to the removal of $C_6H_9O_3$ fragment (Calcd. 20.5, Found 21.1%), while the fourth step is attributed to the removal of $C_7H_5NO_2$ species (Calcd. 21.4, Found 20.5%), followed by the formation of CoO residue at 700 °C (12.7%).

The thermograms of [Pd(Hcs-ba)Cl(H_2O)].$2H_2O$ shows the first step weight loss between 32 and 145 °C, which corresponds to the release of crystal lattice water (Calcd. 5.6 Found 5.4%)[11]. The second decomposition occur between 146 and 370 °C attributes to the loss of cs-unit ($C_6H_{11}NO_4$), coordinated water and 1/2Cl_2 fragments (Calcd. 33.7 Found 34.4%). Two more TG inflections were observed in the ranges 370 – 518 and 519 – 705 °C, may arise from the elimination of C_7H_5NO (Calcd. 18.7,

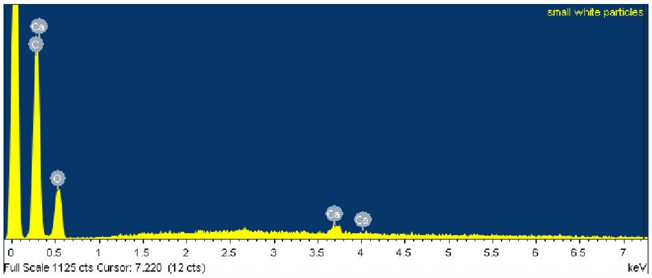


Figure 3a: Matrix of cs

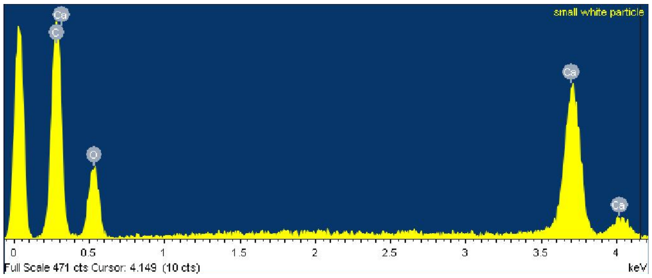


Figure 3b: Matrix of H_2cs-ba

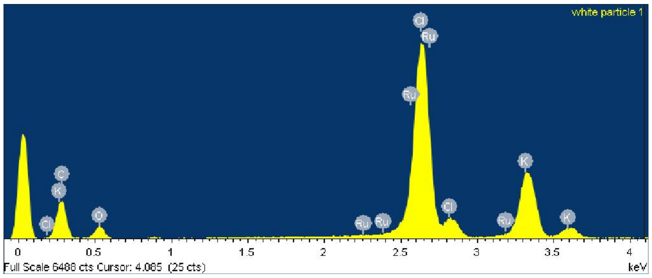


Figure 3c: Matrix of [Ru(Hcs-ba)$Cl_2(H_2O)_2$]

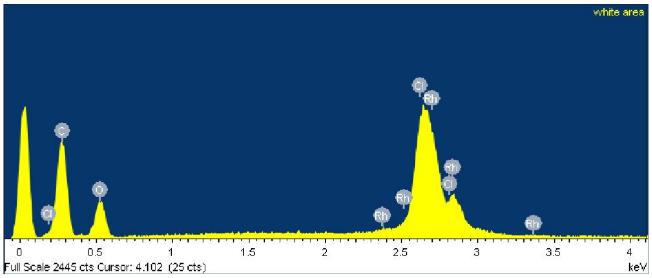


Figure 3d: Matrix of [Rh(Hcs-ba)$Cl_2(H_2O)_2$]

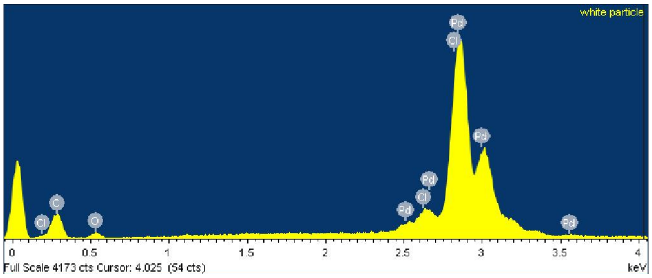


Figure 3e: Matrix of [Pd(Hcs-ba)Cl(H_2O)]

Found 18.8%) and C_5H_9O (Calcd. 13.0, Found 12.4%) fragments, respectively, followed by the formation of PdO residue (24.0%).

Scanning electronic microscopy

The distribution of the particle sizes of (cs), H_2cs-ba, [Ru(Hcs-ba)$Cl_2(H_2O)_2$], [Rh(Hcs-ba)$Cl_2(H_2O)_2$] and [Pd(Hcs-ba)Cl(H_2O)] was estimated and the morphology was studied by scanning electron microscopy, as shown in Figure 3. Chitosan (cs) showed to have a more regular surface and large particle sizes than the Schiff-base modified chitosan (H_2cs-ba)[38,39], due to the chemical modification of cs surface[5]. This modification causes successive reduction on the particles sizes which indicates an apparent increase on the adsorption capacity of the metal ions through complex formation[20]. However, the reduction of the particles sizes is surmounted by the reduction of the free amino groups on the chitosan surface due to Schiff-base formation. In contrast, the surface of [Ru(Hcs-ba)$Cl_2(H_2O)_2$], [Rh(Hcs-ba)$Cl_2(H_2O)_2$] and [Pd(Hcs-ba)Cl(H_2O)] do not exhibit the same morphology of H_2cs-ba. The SEM images of the complexes suggest that on imprinting the metal ions on the modified chitosan could leave out their foot-print increasing the porosities on the surface[40]. This feature may assign to the coordination of the metal ions to H_2cs-ba active sites[5]. Also, the analysis of the matrix indicates the presence of the metal ions (Ru, Rh and Pd) on the surface of the modified polymer (Figure 3).

X-ray diffraction spectroscopy

The great intra-molecular hydrogen bond leads to cs crystalline character that distinguished it from most carbohydrate polymers[41,42]. Figure 5 illustrates the XRD patterns of cs, H_2cs-ba Schiff-base, [Co(Hcs-ba)(AcO)$(H_2O)_2$] and [Pd(Hcs-ba)Cl(H_2O)]. The diffraction pattern of cs shows two characteristic peaks at 2θ = 10.4 and 19.8°, indicating the high degree of crystallinity[15,43]. Whereas, for H_2cs-ba, there is one peak of 2θ = 20.0°, indicating remarkable decrease in crystallinity after grafting with 4-hydroxysalicylidene. H_2cs-ba shows a very weak reflection at 2θ = 6°. The same reflection is observed in XRD pattern of cs-salicylidene Schiff-base[15]. The XRD patterns of [Co(Hcs-ba)(AcO)$(H_2O)_2$] and [Pd(Hcs-ba)Cl(H_2O)] were also appreciably different from that of H_2cs-ba. They show weak reflections at 2θ = 13.4 and 20.1° (in case of Co(II)) and 12.5° (in case of Pd(II)) without any noticeable peaks for pure Co or Pd in the XRD patterns[15].

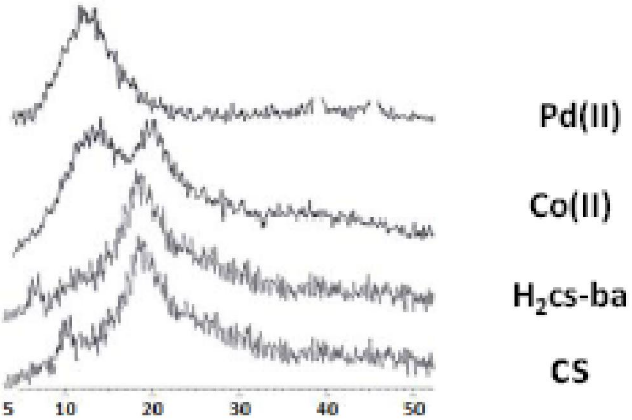


Figure 4 : XRD of cs, H_2cs-ba Schiff-base and its Co(II) and Pd(II) complexes

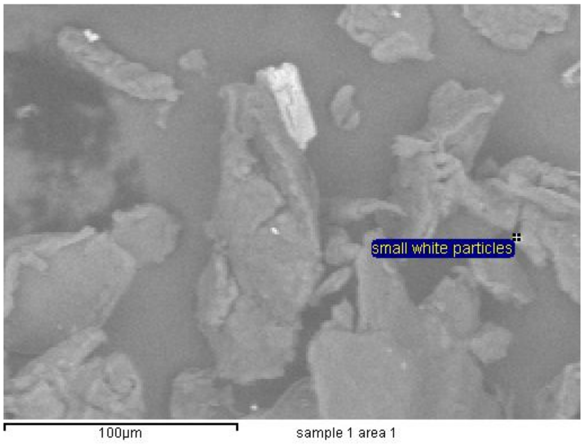


Figure 5a : SEM of cs

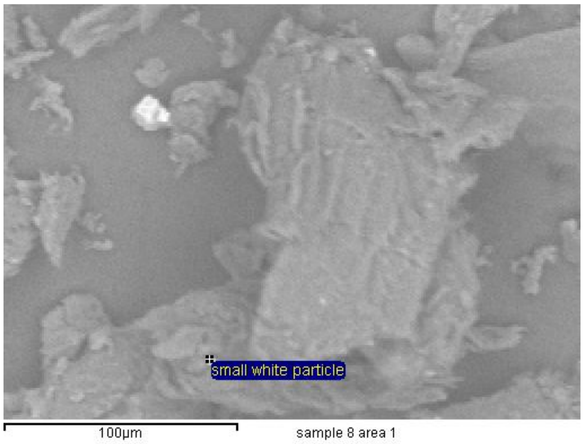


Figure 5b : SEM spectrum of H_2cs-ba

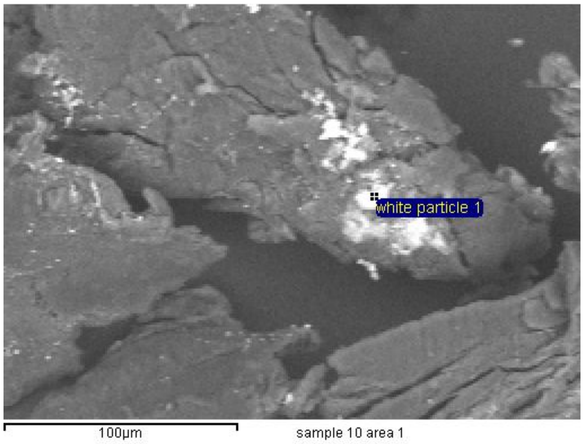


Figure 5c : SEM of $[Ru(Hcs\text{-}ba)Cl_2(H_2O)_2]$

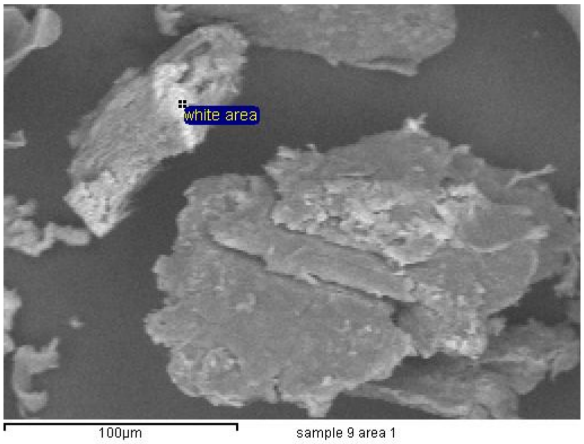


Figure 5d : SEM of $[Rh(Hcs\text{-}ba)Cl_2(H_2O)_2]$

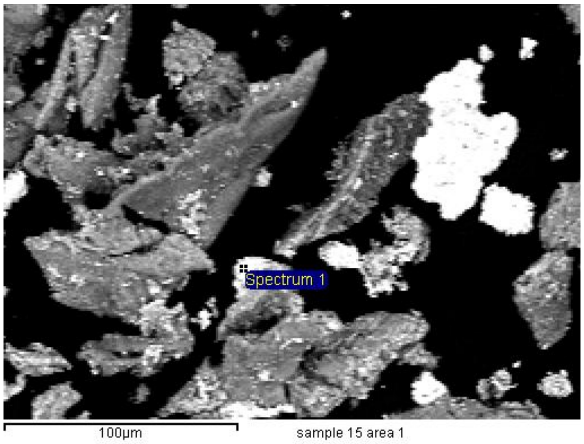


Figure 5e : SEM of $[Pd(Hcs\text{-}ba)Cl(H_2O)]$

Catalytic epoxidation of 1-hexene

The ability of the complexes obtained to catalyze the epoxidation of 1-hexene was systematically examined in the presence of H_2O_2 as co-oxidant; without reductant[9]. Since these modified chitosan Schiff-base complexes are not easily soluble in common solvents, the oxidation processes were carried out under heterogeneous catalysis system.

Generally, linear alkenes such as 1-hexene can be directly oxidized to 1,2-epoxyhexane by H_2O_2 or molecular oxygen at 353 – 373 K without any reductant[9,44]. TABLE 1 shows the catalytic activity of $[M(Hcs\text{-}ba)Cl_2(H_2O)_2]$ (M(III) = Fe, Rh), $[M'(Hcs\text{-}ba)(AcO)(H_2O)_2]$ (M'(II) = Co, Ni) and $[Pd(Hcs\text{-}ba)Cl)H_2O)]$ in the epoxidation of 1-hexene to 1,2-epoxyhexane. The epoxidation of 1-hexene is increased by rising the reaction temperature up to 353 K, as this high temperature initiate the epoxidation process[45] and thus choices to be the experimental temperature. Also, the relation between the epoxidation percentage and the reaction time at 353 K shows that the highest catalytic activity of the complexes under study is observed after 14 hours.

TABLE 1: Catalytic epoxidation of 1-hexene by modified chitosan Schiff-base complexes in the presence of H_2O_2 as co-oxidant at 353 K for 14 hours.

Complexes	First use Yield % (selectivity)	First use TO[a]	Second use Yield % (selectivity)	Second use TO[a]
$H_2cs\text{-}ba$	20 (80)	60	16 (83)	57
$[Ni(Hcs\text{-}ba)(AcO)(H_2O)_2]$	79 (98)	280	70 (99)	265
$[Fe(Hcs\text{-}ba)Cl_2(H_2O)_2]$	93 (99)	301	82 (99)	287
$[Rh(Hcs\text{-}ba)Cl_2(H_2O)_2]$	82 (95)	298	80 (95)	265
$[Pd(Hcs\text{-}ba)Cl(H_2O)]$	65 (55)	254	58 (55)	220

Turnover number is (epoxide/catalyst) in mmol.

All the catalysts reported in this study are found to be stable under experimental conditions as they are recovered by separation, washing with EtOH and Et_2O and drying under vacuum. Also, these catalysts show activity for further catalytic runs (TABLE 1), but they undergo some degradation over 24 h as evidenced by a slight metal loss. The same features have been observed for HY-anchored Fe^{3+}-APTSsal, M-APTSsal (M(II) = Mn, Co, Ni, Cu, Pd), Ag-APTSsal and WO_2^{2+}-APTSsal complexes[9]. The catalytic activities of the filtrates from the washing of the first time use of the catalysts was examined for the re-use, but very poor activities were obtained.

As 1-hexene (linear olefin) can easily approach the catalyst active sites[46], all the reported catalysts in this study are showing high selectivity of 1,2-epoxyhexane formation (93 – 65%) with small amounts of by-products being detected by GC, except for Pd(II) complex (selectivity is 55%). The same feature have been reported for Pd-APTSsal complex[9]. In order to explain the catalytic activity of modified chitosan Schiff-base (H_2cs-ba) complexes for the epoxidation of 1-hexene by H_2O_2, a radical chain mechanism have been proposed after decomposition of hydrogen peroxide to oxygen[9,47].

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