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Synthesis and Catalytic Application of D-Glucose Derived Ytterbium(III) Complex in Biginelli Reaction

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Abstract

4,6-O-Ethylidene-*N*-(2-hydroxybenzylidene)- β -D-glucopyranosylamine has been reacted with ytterbium(III) acetate and the resultant complex has been used as catalyst in the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones (DHPMs). Twenty-one DHPMs have been synthesised under neat reaction condition in appreciable yields (73–96%) and reusability of the catalyst has been established.

Key words : D-Glucose · Lanthanides · Ytterbium · Homogenous catalysis · Biginelli reaction.

1. Introduction

Lanthanide complexes are widely used in the fields of bioimaging [1], molecular sensing [2], magnetic resonance imaging [3], clinical diagnosis [4] and polymer synthesis [5] owing to their unique properties like long-lived luminescence [6], single-molecule magnetism [7], flexible coordination capability [8], Lewis acidity [9] and photosensitivity [10]. Such complexes have also been used as catalysts in several organic reactions like hydrogenation [11], photo induced oxidation reduction [12], polymerization [13] and Diels-Alder reactions [14]. Researchers have established the ligand (monodentate halide ions, bidentate acetate anions, polydentate crown ethers and porphyrins) induced perturbation in the physical and chemical properties of lanthanide complexes [15, 16]. In most of the complexes, lanthanides are coordinated to oxygen atoms of the ligand [17], however, utilization of carbohydrate based ligands are scarce. Rao's group has explored the interaction of mono- and di- saccharides with La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Dy(III) ions [18] while Zhao group reported the crystal structure of Pr(III)(D-rib.5H₂O) [19]. Since, binding abilities of 4,6-Oethylidene-*N*-(2-hydroxybenzylidene)- β -D-glucopyranosylamine (H₃L1) with transition metal ions (Cu(II), Ni(II), Zn(II), V(V), Mo(VI)) alongside U(VI) are known [20], we are interested in exploring the interaction of this ligand with lanthanides and application of the resultant complex in catalysis.

The interaction studies of H₃L1 with trivalent lanthanides in methanol using UV-visible spectroscopy afforded best result for ytterbium(III), which finds various applications in organic syntheses as Lewis acid catalyst [21, 22]. The catalysed reactions include the synthesis of several heterocycles as well as 3,4-dihydropyrimidin-2(1H)-ones/thiones (DHPMs) via Biginelli reaction [23]. DHPMs are extensively used in medicinal field as calcium channel modulators, anti-cancer, anti-inflammatory, anti-microbial and anti-viral agents [24-26]. Inspired from these facts, we reacted the ytterbium(III) acetate with H₃L1 in methanol and isolated the corresponding product. The isolated complex was used as catalyst in Biginelli reaction and

twenty-one heterocycles have been isolated. Hence, this paper deals with the synthesis of glucose derived ytterbium complex and its application as catalyst in the synthesis of DHPMs.

2. Experimental

2.1 Materials and methods

Entire synthetic experiments were performed under normal atmospheric conditions. Ytterbium(III) acetate was purchased from Alfa Aesar, D-Glucose, Acetonitrile and methanol (HPLC grade) from Merck India and all other chemicals along with solvents were procured from local supplier. Solvents were distilled following the standard methods before use. UVvisible spectra were recorded on Jasco V-650 spectrophotometer and data was processed using OriginLab software. ¹H and ¹³C NMR were recorded on a Bruker Avance spectrometer and data was processed using MestReNova 10 software. The IR spectra were recorded on Shimadzu infinity FTIR machine using KBr Matrix and HRMS data on an Agilent 6545 LC-QTOF system. Melting point was recorded in open capillary tubes on EZ-Melt automated melting point apparatus and are uncorrected. HPLC data was collected on Waters binary pump LC system equipped with PDA detector and processed using Empower 2 software at 280 nm. Chromatographic conditions for reverse phase separation are as follows-: Column, Waters Sunfire C18 5µm 4.6×250 mm; Elution method, gradient; Mobile phase, acetonitrile and water; Flow rate, 0.4 mL/min and for chiral separation: Column, Kromasil 5-Amycoat RP $5\mu m 4.6 \times 250 mm$; Elution method, isocratic; Mobile phase, water and acetonitrile (v/v) in the ratio 1: 11; Flow rate, 0.6 mL/min. Elemental composition was obtained from Thermo finnigan FLASH EA 1112 series CHNS(O) analyzer and thermal analysis was performed on Shimadzu TGA-50 in the temperature range of 40-800 $^{\circ}$ C under N₂ atmosphere at heating rate 10 $^{\circ}$ C/min. Powder X-ray diffraction data was aquired using Rigaku Miniflex II with copper anode (Cu-Ka, λ = 1.54 Å) as X-ray source. SEM images and EDX analysis were obtained from Leica ultra microtome EM UC7, FEI Apreo LoVac with Aztec standard EDS system (resolution 127 eV on Mn-K α).

2.2 Synthesis of 4,6-O-ethylidene-N-(2-hydroxybenzylidene)- β –D-glucopyranosylamine (H₃L1).

D-Glucose was converted to 4,6-*O*-ethylidene- β -D-glucopyranosylamine, which was further condensed with salicyaldehyde following the literature procedure to obtain the ligand H₃L1 [27, 28]. The purity of the ligand was established by NMR analysis and HRMS (m/z calcd for C₁₅H₁₉NO₆ (M+H)⁺ = 310.1285; found 310.1285) data.

2.3 Synthesis of ytterbium(III) complex (YbH₃L1)

Methanolic solution of ytterbium(III) acetate (1.1 mmol) was added to a stirring solution of H₃L1 (1 mmol) in methanol at room temperature. The reaction mixture was stirred over night and pale yellow precipitate formed was filtered. The residue (product) was washed with methanol and dried. Yield, 78%; Pale yellow solid; mp, charred above 210 °C; IR (KBr matrix, cm⁻¹): 1631 (v_{C=N}), 1546 (v_{C=O(asym)} of COO⁻), 1454 (v_{C=O(sym)} of COO⁻), 1072 (v_{C-O}); Elemental analysis (weight %): CHNO calculated for Yb(C₁₅H₁₈NO₆)(C₂H₃O₂)_{0.25}(CH₃OH)_{0.5}, C(37.522), H(4.084), N(2.735), O(21.868) found C(38.099), H(4.553), N(2.368), O(21.405); UV-visible peaks: 269 ($\pi \rightarrow \pi^*$), 357 ($\pi \rightarrow \pi^*$) nm [29]; HRMS: m/z calcd for C₄₅H₅₄N₃O₁₈Yb ([Yb(H₃L1)₃+H]⁺) and C₃₀H₃₆N₂O₁₂Yb ([Yb(H₃L1)₂]⁺), 1099.2869 and 790.1657; found 1099.2867 and 790.1659 respectively.

2.4 General procedure for synthesis of 3,4-dihydropyrimidin-2-(1H)-ones/thiones

Ethyl/benzyl acetoacetate (1.0 mmol), aldehyde derivative (1.0 mmol) and urea/thiourea (1.0 mmol) were stirred at 90 °C in presence of YbH₃L1 (1 mol% as per empirical formula) under neat condition. The product solidified within an hour, which was cooled to room temperature and ethanol (3–5 mL) was added to that. The suspension was filtered to isolate the solid product, which was further recrystallised from ethanol.

3. Results and discussion

3.1 Synthesis and characterization of ytterbium complex (YbH₃L1)

4,6-O-Ethylidene-*N*-(2-hydroxybenzylidene)- β -D-glucopyranosylamine (H₃L1) was screened for interaction with trivalent lanthanides using UV-visible spectroscopy. Methanolic solution of H₃L1 (10⁻⁴ M) and lanthanide(III) acetates (10⁻⁴ M) were mixed in 1:1 ratio and UV-visible spectra were recorded for the resultant mixtures. Hypochromic shift in the ligand's band at 319 nm and appearance of a new band at 357 nm indicated the ligand interaction with metal. The stacked spectra of mixtures along with ligand are shown in Fig. 1a, which clearly indicates the major change in case of ytterbium(III) acetate. Inspired from these results, data for Job's plot [30] (Fig. 1b) was generated using the absorbance value of mixtures at 357 nm.



Fig. 1 (a) Absorbance spectra of methanolic solution containing lanthanide acetate and H_3L1 in 1:1 ratio; (b) Job's plot for interaction of Yb³⁺ with H_3L1



Fig. 2 (a) Absorbance spectra for titration of H_3L1 with Yb^{3+} ; (b) Exponential fit titration curve at 357 nm

This study supported the ligand interaction with ytterbium in 1:1 ratio and appearance of isosbestic points during titration of H_3L1 with Yb(III) (Fig. 2a) supported the conservation of stoichiometry in the course of complex formation.

Yoe-Jones method [31] has been used on absorbance values of mixture at 357 nm (Fig. 2b) to obtain the binding constant (K_{est}) of the complex as 1.77 × 10⁶ M⁻¹. This result (log K_{est} = 6.3) is comparable with that of Borisova et al., who have reported log K_{est} values in the range 5.6–8.5 for ytterbium complexes with tetradentate *N*,*N'*,*O*,*O'*-dipyridyl-based ligands [32]. Literature reports on metal ion binding mode of H₃L1 suggests that it can exhibit maximum tetradenticity [33, 34] while ytterbium ought to have more than six coordination number, which indicates the possibility of multinuclear complex formation. In order to further learn about the entity of complex, we isolated the solid product after reacting the ligand and metal salt in 1:1 ratio (details are provided in section 2.3) and explored its composition. FTIR spectrum of the complex exhibited peaks at 1631 and 1072 cm⁻¹ corresponding to $v_{C=N}$ and v_{C-O} stretches of the metal bound ligand. Few peaks also appeared at 1546 and 1454 cm⁻¹, agreeing to $v_{C=O}$ (asym) and $v_{C=O}$ (sym) stretches of metal bound acetate moiety [35] (Fig. S1). This study supported the involvement of both H₃L1 and acetate ion in complexing the ytterbium. Weight percentage of C, H, N, O determined by elemental analysis (mentioned in

section 2.3) tallies with $Yb(C_{15}H_{18}NO_6)(C_2H_3O_2)_{0.25}(CH_3OH)_{0.5}$, which also supports the interaction of metal and ligand in 1:1 ratio. HRMS study of the isolated complex provided peaks at m/z 1099.2867 ($[Yb(H_3L1)_3+H]^+$) and 790.1694 ($[Yb(H_3L1)_2]^+$) supporting the association of ytterbium with two to three ligands which may be possible in multinuclear complex. Fragmentation analysis using collison chamber voltage 20V resulted in daughter ion peaks at 790.1679 (C₃₀H₃₆N₂O₁₂Yb) and 498.0517 (C₁₅H₁₈NO₇Yb) for parent m/z 1099.2867, and at 498.0468 (C₁₅H₁₈NO₇Yb) for parent m/z 790.1694, which supported the above prediction. Differential thermal analysis curve of the complex exhibited five stages of decomposition (Fig. S2), where initial weight loss (2.8%; 40-150 °C) may be due to the elimination of methanol, which is in well agreement with the therotical value (3.1 w%). Combined weight loss for the remaining four steps (62.9%; 150-800 °C) may be attributed to the removal of ligand and acetate ions (calculated 63.1%) leaving Yb₂O₃ as white powder [36]. Crystallinity and particle size distribution of the complex have been calculated as 60% and 34±5 nm (by Scherrer Equation) [37] using Powder X-ray diffraction data (Fig.S3). SEM images revealed rod shaped morphology of the complex with uniform distribution of ytterbium all over the surface (Fig. 3). Several attempts to crystallize the complex failed and hence, actual coordination sphere of the metal centre could not be established.



Fig. 3 SEM (left) and EDX (right) images showing the morphology and ytterbium distribution in YbH₃L1

3.2 Catalytic synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones

Metal complexes of H₃L1 have been used as catalyst in several organic reactions such as Mo(VI) complex in selective oxidation of organic sulfides to sulfoxides, sulfones and alkenes to epoxides while dinuclear Cu(II) complex has been used in selective oxidation of catechol and benzylic alcohols to corresponding carbonyl derivatives [20]. Several reports on ytterbium(III) catalysed reactions are also available, where it has been used in glycosylation [38], cycloadditions [39, 40], hydrophosphonylation [41, 42] along with typical Mannich, Michael, Friedel-Crafts and Diels-Alder reactions [21]. Few reports are also available on ytterbium complex catalysed Biginelli reaction [23] including a report on Schiff base derived complex [43], which prompted us to explore the catalytic action of YbH₃L1 towards Biginelli reaction. Firstly, optimisation of reaction was performed for best suited solvent, temperature, reaction time and catalyst loading using ethyl acetoacetate, benzaldehyde and urea as typical reactants. Progress of reaction was monitered using thin-layered chromatography and yields were calculated by quantitative HPLC seperation. Standard/test solutions required for calculation of yield were prepared by dissolving pure ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4tetrahydropyrimidine-5-carboxylate (B1) or the reaction mixture in 1 mL dimethylsulfoxide, which was further diluted with methanol and calibration curve was plotted using the standard solutions with concentrations 10, 50, 100, 200, 300, 400 and 500 µM. Blank reactions were performed using vtterbium(III) acetate and vtterbium(III) triflate to find the effect of ligand on product formation. Summary of optimisation reactions are presented in Table 1, which validates the optimum conditions as 1 mol % catalyst loading with reaction time and temperature as 90 °C and one hour respectively under neat condition (Scheme 1).



Scheme 1 Optimised protocol for YbH₃L1 catalysed synthesis of DHPMs

Entry	Catalyst (mol %) ^b	Solvent	Yield ^c (%)	Time (h)	Temperature (°C)
1	YbH ₃ L1 (1.0)	ACN	16	1	reflux
2	YbH₃L1 (1.0)	DCM	53	1	reflux
3	YbH ₃ L1 (1.0)	DMF	83	1	reflux
4	YbH₃L1 (1.0)	Ethanol	65	1	reflux
5	YbH ₃ L1 (1.0)	Water	55	1	reflux
6	YbH₃L1 (1.0)	Neat	98	1	90
7	YbH ₃ L1 (0.5)	Neat	64	1	90
8	YbH ₃ L1 (2.0)	Neat	96	1	90
9	YbH ₃ L1 (3.0)	Neat	93	1	90
10	YbH₃L1 (10.0)	Neat	67	1	90
11	YbH ₃ L1 (1.0)	Neat	39	0.25	90
12	YbH₃L1 (1.0)	Neat	64	0.5	90
13	YbH ₃ L1 (1.0)	Neat	85	0.75	90
14	YbH₃L1 (1.0)	Neat	97	1.5	90
15	Yb(OTf) ₃ (1.0)	Neat	62	1	90
16	Yb(CH ₃ COO) ₃ (5.0)	Neat	25 ^d	1	90
17	Yb(CH ₃ COO) ₃ (5.0)	Neat	37	12	90
18	Yb(CH ₃ COO) ₃ (5.0)	Neat	39	24	90
19	YbH ₃ L1 (1.0)	Neat	traced	1	RT
20	YbH₃L1 (1.0)	Neat	37	4	RT
21	YbH₃L1 (1.0)	Neat	42	24	RT
22	YbH₃L1 (1.0)	Neat	traced	1	50
23	YbH ₃ L1 (1.0)	Neat	28 ^d	1	70

Table 1 Optimisation of conditions for ytterbium complex catalysed Biginelli reaction^a

^a ethyl acetoacetate (1 mmol), urea (1 mmol), benzaldehyde (1 mmol)
 ^b mole percentage with respect to benzaldehyde
 ^c yield by HPLC
 ^d isolated yields

Under optimum reaction conditions set by us, twenty-one different DHPMs were synthesised in good to excellent yields (73–96%) and all the molecules were characterized with the help of NMR and HRMS analysis (Table 2). Aldehydes bearing electron donating groups (EDG) afforded lower yields while opposite drift was observed in case electron withdrawing substituents and similar trend was reported by Zhang et al. [44]. Increase in the number of EDGs on aldehyde (entry B7, B8), further decreased the yield as expected. Replacement of urea with thiourea also resulted in the lowering of corresponding product formation, which complies with the results reported by Wang & co-workers [45, 46]. While working with ytterbium triflate, they reported the completion time for Biginelli reaction as 20 min in case of urea [45] and one hour for thiourea [46]. Reusability of the catalyst was tested with ethyl acetoacetate, benzaldehyde and urea following the synthetic method mentioned in section 2.4. After completion of first cycle, product was isolated from ethanol and the filtrate was evaporated under reduced pressure to result in slurry of catalyst, which was charged with fresh reactants to perform the second cycle of reaction. This procedure was repeated for five times to ensure the recyclability of catalyst and result is shown in Fig. 4. During recycling process, no appreciable loss in the catalytic activity was detected, contrary increase in efficiency was noticed in the course of first few cycles, which may be due to the trapping of reactants from previous cycle.



Fig. 4 Recyclability result of YbH₃L1 catalysed Biginelli reaction

Entry	R	R'	Х	Yield(%) ^b
B1	Ethyl	phenyl	0	92
B2	Ethyl	2-chlorophenyl	0	95
B3	Ethyl	3-chlorophenyl	0	94
B4	Ethyl	4-chlorophenyl	0	95
B5	Ethyl	3-chloro-2-fluorophenyl	0	96
B6	Ethyl	4-bromo-2-fluorophenyl	0	96
B7	Ethyl	3,4,5-tri-methoxyphenyl	0	87
B 8	Ethyl	2,4,6-tri-methoxyphenyl	0	82
B9	Ethyl	4-methylphenyl	0	94
B10	Ethyl	4-hydroxyphenyl	Ο	80
B11	Ethyl	4-methoxyphenyl	0	90
B12	Ethyl	4-bromophenyl	0	89
B13	Ethyl	styryl	0	91
B14	Ethyl	1-naphthyl	0	90
B15	Ethyl	thiophene-2-yl	0	82
B16	Ethyl	phenyl	S	78
B17	Ethyl	2-chlorophenyl	S	85
B18	Ethyl	4-chlorophenyl	S	83
B19	Benzyl	phenyl	0	90
B20	Benzyl	phenyl	S	73
B21	Ethyl	2-hydroxyphenyl	0	92

Table 2 Synthesis of DHPMs using ytterbium complex under optimised reaction conditions^a

^a Aldehyde (1.0 mmol), urea/thiourea (1.0 mmol), acetoacetic ester (1.0) and ytterbium complex (1 mol%) at 90 °C, neat condition, 1 hour.

^b isolated yield

.

A comparison of our protocol with previous literature reports on ytterbium catalysed Biginelli reaction has been summarized in Table 3. Current catalytic system has advantages over other methodologies in terms of catalyst loading, reaction time as well as purification process. The current catalyst has been reused for five times without appreciable loss in activity. Ytterbium complex catalysed Biginelli reaction with 2-hydroxybenzaldehydes often leads to the formation of oxygen-bridged tricyclic tetrahydro pyrimidines [43], but we have noticed the formation of mainly Biginelli product. Since, H₃L1 is chiral in nature, we were expecting the enantioselective product, but unfortunately, we noticed the formation of racemic mixture, which was supported by chiral HPLC analysis (Fig. S5c).

Entry	Catalyst (mol %)	Time	Solvent	Temperature	Reference
1	Yb(OTf) ₃ (5 mol%)	1 h	Neat	100°C	[45, 46]
2	Resin bound Yb3+	48 h	Neat	120°C	[47]
3	Yb(OTf)₃ (20 mol%)	12 h	Toluene	Reflux	[48]
4	Yb(CH ₃ SO ₃) ₃ (10 mol%)	-	Ethanol	Reflux	[49]
5	Yb(OTf) ₃ +Lª (5 mol%)	20-30 h	THF⁵	RT	[50]
6	Yb(NPf ₂) ₃ (1 mol%)	2-6 h	$C_{10}F_{18}$	90°C	[51]
7	YbCl ₃ (3 mol%)	3 h	Neat	90°C	[44]
8	Yb(pic) ₃ .L ^a (10 mol%)	60 h	THF⁵	RT	[43]
9	Yb(PFO) ₃ (5 mol%)	4 h	Neat	120°C	[52]
10	Yb.H ₃ L1 (1 mol%)	1 h	Neat	90°C	This report

Table 3 Comparison of Biginelli reactions catalysed by different ytterbium compounds

^a L represents the ligand used in respective reference

^b Tetrahydrofuran

Conclusion

This is the first report where 4,6-*O*-ethylidene- β -D-glucopyranosylamine derived ligand has been screened for interactions with lanthanides. Based on the interaction results, synthesis of glycoconnjugate derived Yb(III) complex has been executed and further the product has been used as catalyst in Biginelli reaction. Totally twenty-one 3,4-dihydropyrimidin-2-(1H)-ones/thiones derivative have been synthesised and the stability of catalyst has been established via five times recycling process. After optimisation, we have performed the catalytic reaction under neat condition with 1 mol% catalyst loading, and synthetic protocol aligns with the green synthesis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at XXXXXXXXXX.

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Synthesis and Catalytic Application of D-Glucose Derived Ytterbium(III)

Complex in Biginelli Reaction

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Highlights

- First report on lanthanides interaction with glucopyranosylamine derivative
- Application of N-glycoconjugate derived Yb(III) complex in Biginelli reaction
- Neat synthesis of twenty-one 3,4-dihydropyrimidin-2(1H)-ones/thiones
- Catalyst has been recycled for five times without appreciable loss in activity

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Not required..

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Vimal Kumar Madduluri: Conceptualization, Methodology, Investigation, Data curation, Writing - Original Draft

Santosh Kumar Mishra: Formal analysis, Investigation, Data curation

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