

# Investigating the effect of immobilization of yttrium-Schiff base onto magnetite nanoparticles: enhanced catalytic activity in the synthesis of dihydropyrimidinones under solvent-free conditions

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**Abstract** A new complex of yttrium-salpr was synthesized through the reaction of  $Y(NO_3)_3 \cdot 6(H_2O)$  and salpr Schiff base (salpr = N,N'-bis(3-salicylidenaminopropyl) amine). The prepared complex was characterized by Mid and Far-IR, <sup>13</sup>C-NMR, <sup>1</sup>H-NMR, UV–Vis, XRF, and CHN. The obtained data suggested a binuclear structure for this compound. To our surprise, the catalytic activity of this complex was even lower than its precursor,  $Y(NO_3)_3 \cdot 6(H_2O)$ , in one-pot synthesis of dihydropyrimidinones under solvent-free conditions. As one of the reasons of this reduced activity should pertain to the binuclear structure of the complex that reduces the availability of yttrium in the reaction, the complex was immobilized on modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles, which not only increases the surface to the volume ratio of the compound, but also hinders the formation of binuclear structure due to site (Schiff base) isolation. These prepared nanoparticles depicted noticeably high catalytic activity as well as good recyclability and very easy separation.

**Keywords** Yttrium · Heterogeneous and homogeneous catalysis · Immobilization · Schiff base · Nanostructures

# Introduction

Yttrium is a major constituent of the mineral-containing middle or heavy earth group. It tends to occur in the same deposits as the lanthanides due to the similar ionic radius of  $Y^{3+}$  to  $Ho^{3+}$  and  $Er^{3+}$  [1]; however, yttrium is more abundant and less toxic than almost any other lanthanide element. Different compounds of yttrium have shown great catalytic activity; yttrium nitrate hexahydrate Y(NO<sub>3</sub>)<sub>3</sub>·6(H<sub>2</sub>O)

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was found to be an efficient catalyst for the one pot synthesis of dihydropyrimidinones (DHPMs), named the Biginelli reaction [2]. Ever since this reaction was discovered by the Italian chemist Pietro Biginelli [3], scientists have paid a great deal of attention to it due to the unique biological activities of Biginelli compounds. These are antihypertensive, antiviral, antitumor, antibacterial and antiflammatory agents [4], which are also the basic skeleton of some pharmaceuticals that are used to prevent or treat cancer and AIDS [5]. The first used catalyst in this reaction was HCl [3]. To date, a broad spectrum of catalysts, including ammonium chloride [4], Lewis acids (yttrium(III) acetate [6], Lanthanide Triflate [7]), heteropolyacids (doped Keggin [8], Wells–Dawson acid [9]), and organic–inorganic hybrid materials [10], have been studied in this reaction to increase yield, ease reaction conditions, lower temperature, shorten reaction time, or make the reaction environmentally friendly.

Y(III) strongly interacts with hard bases, and makes strong complexes with oxygen and nitrogen. Hence, Schiff bases can be considered very good ligands for vttrium(III) [11], while their complexes have shown good catalytic activity in different reactions such as ring opening polymerization [12] and transacylation [13]. However, many metal Schiff base complexes tend to form dimeric per-oxo or u-oxo species that decrease or deactivate the catalytic activity [14]. Moreover, recycling these catalysts is often tedious and time consuming. For overcoming the aforementioned drawbacks, Schiff base complexes are immobilized onto different solid supports. Silica-coated magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (SCMNPs) are one of the newest discovered solid supports of the very recent decades. The magnetite nanoparticles have superparamagnetic properties that enable them to be attracted to an external magnetic field, but retain no residual magnetism after removing the magnetic field [15]; moreover, formation of a silica layer on the surface of magnetic nanoparticles could screen the magnetic dipolar attraction between magnetic nanoparticles, which favors the dispersion of magnetic nanoparticles in liquid media [16].

In this study, we synthesized and characterized a new complex of Y(III) **1** by condensation of yttrium nitrate hexahydrate and salpr Schiff base. The analytic data revealed a binuclear structure where Y(III) centers were bridged by two phenoxooxygens. Then, the catalytic activity of this complex was investigated in one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones under solvent-free conditions. The results were in contrast with our expectations when the catalytic activity of the prepared complex was lower than with yttrium nitrate as the precursor. We assumed that this decrease in catalytic activity was due to the binuclear structure and steric hindrance around yttrium(III). Hence, we attempted to synthesize **2** and immobilize this complex onto SCMNPs, not only to increase the catalytic activity but also to ease the recyclability. Interestingly, the prepared  $Y^{3+}$  nanoparticles showed great activity in one-pot synthesis of Dihydropyrimidinones under solvent-free conditions.

# Experimental

### Materials and methods

Yttrium nitrate hexahydrate, diethylenetriamine, salicylaldehyde, triethylamine, ferrous chloride tetrahydrate, ferric chloride hexahydrate, and tetraethyl orthosilicate were purchased from Merck Chemical Company and utilized without any more purification. Ammonia (25 %) was obtained from Dr. Mojallali Chemical Laboratories Co., Ltd, Iran. All water utilized in the experiments was doubly distilled.

Infrared (IR) spectra were recorded on an ABB FTLA 2000 spectrometer using KBr pellets. Elemental analyses (C, H and N) were performed using a Perkin-Elmer CHN 2400 elemental analyzer. X-ray fluorescence (XRF) data were obtained on PHILIPS model PW1480. A double-beam spectrophotometer (Shimadzu, UV-240) was used for the UV–Vis absorption determination. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra (300 MHz) were measured in DMSO solutions. Field emission scanning electron microscopy (FE-SEM) images were obtained on a Hitachi S-4160, Japan. Magnetic susceptibility measurements were carried out at room temperature using a vibrating sample magnetometer (VSM), MDK6 Iran. Atomic force microscopy (AFM) images were obtained on a DME 95-50E. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a Zeiss EM 900 instrument with an accelerating voltage of 80 kV.

## Synthesis of 1

Schiff base of Salpr was prepared based on the literature [17]. The synthesis of the complex **1** was performed according to the procedure employed by Wu et al. [18].  $Y(NO_3)_3 \cdot 6(H_2O)$  (0.191 g, 0.5 mM) and triethylamine (0.3 mL) in EtOH (10 mL) were added to a stirred solution of salpr (0.5 mM) in EtOH (10 mL). Yellow sediment was generated rapidly. The precipitate was washed with ethanol and ether, and then dried.

# Synthesis of 2

SCMNPs/salpr was prepared according to the literature [15]. For preparation of **2**, the excess amount of  $Y(NO_3)_3 \cdot 6(H_2O)$  (574 mg, 1.5 mmol) was dissolved in ethanol (50 ml). SCMNPs/salpr (1 g) was sonicated in ethanol (20 ml) for 10 min, added to  $Y(NO_3)_3 \cdot 6(H_2O)_6$ , and refluxed for 12 h. After separation with an external magnet, the product was washed with methanol to remove unreacted  $Y(NO_3)_3 \cdot 6(H_2O)$ .

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

A mixture of catalyst, benzaldehyde, ethyl acetoacetate and urea with mole ratio (0.05 or 0.02:1:1:1.1), was heated under stirring under solvent-free condition. The

reaction was monitored by thin-layer chromatography (TLC) using ethyl acetate/ hexane (4:6) as eluent. After completion, the reaction mixture was washed with water. Finally, the mixture was dissolved in hot EtOH. In the case of using **1** as catalyst, the mixture was suction filtered. For **2**, the catalyst was concentrated on the side wall of the reaction vessel using an external magnet and washed with ethanol. The crude product was recrystallized from EtOH. All products were known compounds and were characterized by comparison with reported values.

### **Results and discussion**

#### **Characterization of 1**

#### FT-IR

The Main FT-IR absorption bands of **1** and its corresponding Schiff base ligands are shown in Fig. 1, and the numbers are given in Table 1. In the spectra of the Schiff base ligand, a strong band occurring at 1633 (s) cm<sup>-1</sup> due to C=N stretching is found to be shifted to lower frequency in **1**, viz., 1630, indicating coordination through azomethine nitrogens. The absorption bands of covalent nitrate with  $C_2v$  symmetry in the complex are observed at five different frequencies. The difference between v1 and v4 is 202 cm<sup>-1</sup>, which is associated with bidentate nitrate coordination [19].



Fig. 1 FT-IR spectra of **a** free salpr Schiff base, **b** 1 in the range of 400–4000 cm<sup>-1</sup>, and **c** 1 in the range of 300–400 cm<sup>-1</sup>

Compound	C=N	Phenolic C–O	Y-0	Y-0-Y	-NH-	–OH	NO <sub>3</sub> (	coordina	nted)		
Free ligand (salpr)	1633	1278	_	-	-	3417	ν1	ν4	ν2	v3	ν5
1	1630	1282 1308	463	303 333 370	3271	3429	_ 1545	_ 1343	_ 1036	- 860	- 791

Table 1 Main FT-IR absorption bands of 1 and salpr (cm<sup>-1</sup>)

Two phenolic C–O stretching vibrations at 1282 and 1308 cm<sup>-1</sup> (Table 1) are found for complex **1** that show they are not in a similar environment. The higher frequency peak is related to phenolic C–O and yttrium interaction [20]. The lower frequency peak at 1282 cm<sup>-1</sup> indicates that some of the oxygen atoms are affected much more strongly by the Y(III), and are coordinated to two yttriums at the same time [20, 21]. The Far-Ir spectrum exhibits vibrational modes at 303, 333, and 370 cm<sup>-1</sup> characteristic of Y–O–Y stretching [22].

A weak band observed at around 463 cm<sup>-1</sup> due to Y–O provides an additional evidence for the coordination of oxygen to Y in this complex. Besides, the band observed at 3271 cm<sup>-1</sup> is due to the presence of secondary amine (–NH–) in the complex. This peak does not exist in the free ligand, probably due to the hydrogen bonding. A broad band at 3429 cm<sup>-1</sup> in **1** is attributed to OH group of the crystal water molecules. This indicates existence of water of hydration [23].

#### NMR

The <sup>1</sup>H-NMR spectrum of the prepared complex **1** exhibits the following signals in DMSO.  $\delta = 8.19$  (s, 4H, CH=N), 6.44–7.21 ppm (m, 16 H, Ar–H), and 2.4–3.8 ppm (complex multiplet, about 16H, CH<sub>2</sub>). Compared to free salpr ligand, the complex depicts the disappearing of the phenolic signal and an upfield shift of azomethine (from 8.50 ppm [14] to 8.19 ppm), which indicate the coordination of phenolic oxygen and azomethine nitrogen to Y atom. Other signals, i.e., those due to aromatic and CH<sub>2</sub> protons, appear at nearly the same position as the free ligand.

Table 2         UV–Vis data of 1 and salpr		λ <sub>max</sub> (nm)	Assignment
	Salpr	264	$\pi  ightarrow \pi^*$
		312	$n \rightarrow \pi^*$
	1	271	$\pi \rightarrow \pi^*$
		354	$n \rightarrow \pi^*$

The <sup>13</sup>C-NMR spectrum of **1** is in agreement with <sup>1</sup>H-NMR. It depicts the following signals in DMSO.  $\delta = 166.6$  ppm (HC=N), 112.7–166.0 ppm (Aromatic Ar–H), 60.3 ppm (–CH<sub>2</sub>–N–), and 49.0 ppm (–CH<sub>2</sub>–C=N–).

### UV-Vis

Table 2 provides electronic spectra of the prepared complex 1, along with its assignments. The electronic absorption spectra of the free ligand and the complex were measured in DMF at room temperature. The free ligand exhibited two bands between 264 and 312 nm due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  ligand transitions. However, in yttrium complex, these bands were found to be shifted toward higher wavelengths (red shift) that support the coordination of the ligand with the metal atom [24].

### Elemental analyses

Efforts to make a single crystal of this complex were unsuccessful. However, Wu et al. synthesized and characterized a complex of yttrium(III) and bis(N-salicylidene)-3-oxapentane-1,5-diamine (a Schiff base similar to salpr) [18]. Single-crystal X-ray structure determination of this complex revealed that the  $Y_2L_2(NO_3)_2 \cdot 2H_2O$  formula of the complex had a centrosymmetric neutral homobinuclear entity with two adjacent moieties coupled together via two phenolato bridges belonging to the two ligands. Based upon the argument given above and also taking into consideration that the IR spectrum proved the presence of two kinds of phenolic C–O bond with yttrium and Y–O–Y bands, the proposed structure for **1** is shown in Fig. 2.

For further investigation, the elemental analysis of the **1** was compared to the proposed structure (Table 3). Interestingly, they were in good agreement, which could prove the correctness of the proposed structure.



Fig. 2 The proposed structure for 1

Tuble 5 Elemental analysis of 1									
Y % <sup>a</sup>	N %	C %	Н %						
18.23	11.54	44.41	4.43						
18.24	11.50	44.37	4.55						
	Y % <sup>a</sup> 18.23 18.24	Y % <sup>a</sup> N %           18.23         11.54           18.24         11.50	Y % <sup>a</sup> N %         C %           18.23         11.54         44.41           18.24         11.50         44.37						

Table 3 Elemental analysis of 1

<sup>a</sup> Obtained by XRF

### **Characterization of 2**

#### FT-IR

In order to confirm the modification of the magnetite surface, the FT-IR spectra of the prepared SCMNPs/salpr and **2** were obtained (Fig. 3; Table 4). Two bands at 454–590 cm<sup>-1</sup> indicate the presence of  $Fe_3O_4$  in the prepared nanoparticles. The silica coating of magnetite nanoparticles was confirmed by observation of a band at 1079 cm<sup>-1</sup> assigned to Si–O–Si and Si–OH stretching vibrations [15].

In the FT-IR spectrum of SCMNPs/salpr a band at 1629 cm<sup>-1</sup> was assigned to C=N stretching vibration. Upon reaction with  $Y(NO_3)_3 \cdot 6H_2O$ , it shifted to lower frequency (1620 cm<sup>-1</sup>), indicating the complexation of C=N group of supported ligand with yttrium. The presence of phenolic C–O in the supported free ligand is confirmed by a peak at 1280 cm<sup>-1</sup> that shifted to 1295 cm<sup>-1</sup> after complexation. As



Fig. 3 FT-IR spectra of **a** free supported salpr Schiff base, **b** 2 in the range of 400–4000 cm<sup>-1</sup>, and **c** 2 in the range of 300–400 cm<sup>-1</sup>

Compound	Fe <sub>3</sub> O <sub>4</sub>	SiO <sub>2</sub>	C=N	Phenolic C–O 1280	Y-0	NO <sub>3</sub> (coordinated)				
SCMNPs/salpr	454 590 350	1079	1629			ν1 -	v4 _	v2 -	v3 -	v5 -
2	454 590 350	1079	1620	1295	a	1548	1350	a	800	a

Table 4 IR spectra of SCMNPs/salpr and its corresponding yttrium complex of 2

<sup>a</sup> Overlap with the broad peaks of  $Fe_3O_4@SiO_2$ 

discussed, the C–O stretching vibration increases on yttrium complex formation [20, 21]. It is worth mentioning that the band indicating the interaction between the oxygen of C–O and two yttriums does not exist here (around 1280 cm<sup>-1</sup> [20]). Besides, the far-IR spectrum exhibits a broad vibrational mode at 350 cm<sup>-1</sup> characteristic of Fe<sub>3</sub>O<sub>4</sub>; however, Y–O–Y bands are not depicted [22]. Hence, it can be inferred that the structure of **2** is different from its binuclear structure in the homogeneous form. Appearance of three bands at 800, 1350, and 1548 cm<sup>-1</sup> proves the presence of covalent nitrate with C<sub>2</sub>v symmetry in the complex [19] (other bands



Fig. 4 The sequence of events in the preparation of 2

of coordinated nitrate overlap with the bands of the support and cannot be seen here). The proposed structure for 2 is depicted in Fig. 4.

### FE-SEM, AFM, and TEM

In order to investigate the morphology and the size of the prepared nanoparticles TEM, FE-SEM, and AFM analyses were conducted (Fig. 5). These images clearly show that these nanoparticles have quasi-spherical morphologies, which is due to the spherical shape of  $Fe_3O_4$  as the core of the nanoparticles with some agglomeration; in fact, in spite of coating the particles with silica, the modified silica coated magnetic nanoparticles still face coagulation as each particle is like a magnet which attracts other particles. On the other hand, it has been proven that if the specimen is magnetic, its magnetic field will deviate the electron beam of TEM



Fig. 5 a TEM, and its corresponding histogram, b FE-SEM, and c AFM images of 2

instrument as it passes through and then the electrons that are used to form TEM images will not be on the optic axis. All the images will be severely aberrated and shift when the operator tries to focus on them [25].

However, to estimate the particle size, the histogram related to TEM was drawn and compared to AFM. The results were in good agreement and showed that the particle sizes are about 10–12 nm.

VSM

Magnetic properties of the prepared nanoparticles were investigated at room temperature by using vibrating sample magnetometry (VSM). Magnetization curve of SCMNPs and the prepared complex are shown in Fig. 6. It exhibited no hysteresis loop and remanence effect, which proves its superparamagnetic properties. This property is critical for its application, since it prevents aggregation and enables particles to re-disperse rapidly when the magnetic field is removed. As it is shown in Fig. 6, the saturation magnetization of SCMNPs is about 48 emu/g that is reduced to 36 emu/g in **2**.

# Elemental analysis

Yttrium content of the prepared nanomaterial was found to be 0.65 wt% on the basis of XRF.

# Catalytic activity

As  $Y(NO_3)_3 \cdot 6H_2O$  has shown good catalytic activity in one pot synthesis of 3,4-Dihydropyrimidin-2(1*H*)-ones, owing to the empty orbitals of  $Y^{3+}$  that stabilize the



Fig. 6 Magnetization curves of a SCMNPs, b 2

acylimine intermediate [2], we decided to evaluate 1 and 2 in this reaction. The reaction procedure is illustrated in Fig. 7.

The obtained data are listed in Table 5. Entries 4 and 5 show the catalytic performance of 1. These data depict the lower catalytic activity of 1 compared to  $Y(NO_3)_3 \cdot 6H_2O$  (entries 2 and 3). This reduction can be discussed from two perspectives. Firstly, according to the proposed structure for 1,  $Y^{3+}$  groups are hindered by Schiff bases and are not easily available to react in the catalytic reaction. Secondly, reducing the electron-withdrawing nitrate groups in 1 compared to  $Y(NO_3)_3 \cdot 6H_2O$  could lessen the Lewis acidic property, and lead to decreasing its catalytic activity. The reaction was also conducted at 90 °C (entries 6 and 7). Although the catalytic activity increased at higher temperature, the yields remained relatively low.

Interestingly, the same reaction with sample 2 depicted high yields of product (entries 9 and 10) compared to both 1 and  $Y(NO_3)_3 \cdot 6H_2O$ . This phenomenon is attributed to immobilization of the yttrium complex onto silica coated magnetite nanoparticles. The newly prepared nanoparticles have higher surface area; hence, there is increased catalytic activity as more catalytic reactions can occur at the same time. Moreover, it can be suggested that site (Schiff base) isolation, due to primary immobilization of Schiff base on to SCMNPs, hinders the formation of binuclear complexes after adding the yttrium salt, which leads to increasing the catalytic activity of 2 in comparison with 1. Another advantage of 2 is very easy recovery and reusability. After each run, the used catalyst was separated from the reaction mixture by means of a permanent magnet, washed and reused in the same catalytic reaction. The recycled catalyst after each run was characterized by IR. It showed characteristic peaks similar to the original unused catalyst. Entry 10 depicts the recyclability of 2 for three cycles.

In order to study the generalizability of the catalytic procedure for 2, a variety of benzaldehyde derivatives with different electronic properties were used. The results showed that both electron-donating and electron-withdrawing groups afforded high yields of the desired products (Fig. 8).



Fig. 7 Synthesis of 3,4-Dihydropyrimidin-2(1H)-ones using 1 and 2

Entry	Catalyst	Mol%	Temp. (°C)	Isolated yield <sup>b</sup> (%)
1	No catalyst <sup>a</sup>	_	70	28 [2]
2	Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	5	70	97 [2]
3	Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	2	70	77 [2]
4	1	5	70	56
5	1	2	70	44
6	1	5	90	63
7	1	2	90	48
8	2	5	70	43
9	2	5	90	95
10	2	2	90	88, 88, 83 <sup>c</sup>

 Table 5
 Effect of catalysts under different reaction conditions for condensation of benzaldehyde, ethyl acetoacetate and urea

Reaction condition: benzaldehyde (5 mmol), ethylacetoacetate (5 mmol), urea (5.5 mmol), in 20 min <sup>a</sup> 60 min

<sup>b</sup> All products were identified by their melting point in comparison with known samples [26]

<sup>c</sup> Catalyst was recycled for three times





# Conclusions

In this study, a novel binuclear complex of yttrium(III) was synthesized. In order to enhance the catalytic activity of this complex in one-pot synthesis of dihydropyrimidinones under solvent-free conditions, it was immobilized onto SCMNPs. The newly prepared nanoparticles not only showed high activity, but also were recyclable and could be separated fast and easily from the reaction mixture.

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