Communication

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Mn-[4-Chlorophenyl-Salicylaldimine-Methylpyranopyrazole]Cl_2 as a Novel Nanostructured Schiff Base Complex and Catalyst

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Mn-[4-chlorophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 ([Mn-4CSMP]Cl_2) as nano-Schiff base complex was prepared and fully characterized by Fourier transform infrared spectroscopy, X-ray diffraction, thermal gravimetric analysis, derivative thermogravimetry, scanning electron microscopy, energy-dispersive X-ray analysis, and UV–vis spectroscopy. The reactivity of nano-[Mn-4CSMP]Cl_2 as a catalyst was tested on the tandem cyclocondensation–Knoevenagel condensation–Michael reaction between phenylhydrazine and ethyl acetoacetate with various aromatic aldehydes to give 4,4′-(arylmethylene)-bis-(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s derivatives.

Keywords: Schiff base complex; Pyranopyrazole; Bis(pyrazolyl)methane; Tandem reaction.

INTRODUCTION

Recently, because of the presence of heterocyclic compounds in many natural products and their applications in pharmacological chemistry, researchers have been devoting much effort to the synthesis of similar compounds and their derivatives using multicomponent reactions (MCRs). MCRs are characterized by clean reaction conditions, high atom economy, and the combining of many complex reactions in effectively one step.[1–8]

Schiff base compounds are widely studied as an important class of ligands due to their easy and convenient protocols of preparation and their interesting coordination chemistry.[9] Schiff base or azomethine ligands are among the principal chelating systems in bioinorganic and various related natural biological processes, and often the coordination chemistry of several forms of Schiff bases is studied extensively. Schiff bases are introduced as ligands to prepare coordination complexes with metal ions and used to prepare catalysts.[10–16]

In the presented work, we have prepared and characterized nano-Mn-[4-chlorophenyl-salicylaldimine-methylpyranopyrazole]Cl_2 (nano-[Mn-4CSMP]Cl_2), whose proposed structure is shown in Figure 1. Nano-[Mn-4CSMP]Cl_2 was successfully used as an efficient catalyst for the tandem cyclocondensation–Knoevenagel condensation–Michael reaction of phenyl hydrazine, ethyl acetoacetate, and aryl aldehydes to give bis(pyrazolyl) methanes (Scheme 1).

RESULTS AND DISCUSSION

Nano-[Mn-4CSMP]Cl_2 was prepared by the reaction of 4-chlorobenzaldehyde with ethyl acetoacetate, malononitrile, and hydrazine hydrate to obtain the related pyranopyrazole according to previous literature,[17] which was then reacted with salicylaldehyde and $MnCl_2.4H_2O$ in ethanol to afford nano-[Mn-4CSMP]Cl_2 as a nano-Schiff base complex (Scheme 2). The structure of nano-[Mn-4CSMP]Cl_2 was confirmed by infrared (IR) spectroscopy, X-ray diffraction (XRD), energy-dispersive X-ray (EDX) analysis, thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), UV–vis spectroscopy, and elemental analysis (CHN).

The IR spectrum of the catalyst showed a broad peak at 2100–3500 cm^{-1}, which could be related to the O–H stretching of OH group, and the peak observed at 1670 cm^{-1} corresponds to the stretching mode of C═N bond of azomethine.

As shown in Figure 2, the XRD patterns of nano-[Mn-4CSMP]Cl_2 has diffraction peaks corresponding to a highly crystalline nature at about $2\theta \approx 11.3°$, 17.0°, 21.4°, and 26.8°. The crystallite size was obtained by the Debye–Scherrer formula $D = K\lambda/(\beta\cos\theta)$. The crystallite size obtained using this formula was at about 23.35 nm (for the highest diffraction line at 26.8°), and inter-planar distance was calculated via the Bragg equation: $d(hkl) = \lambda/(2\sin\theta)$, which gave a value of

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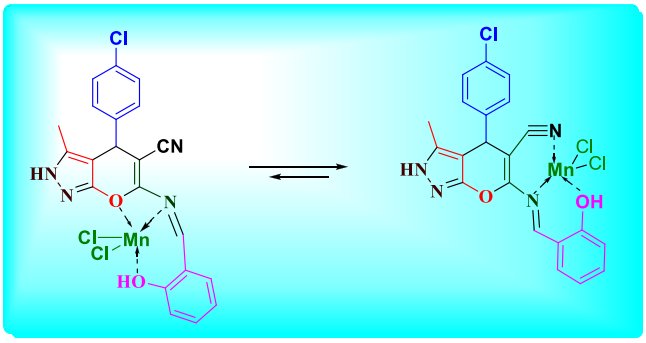


Fig. 1. Proposed structures of nano-[Mn-4CSMP]Cl_2.

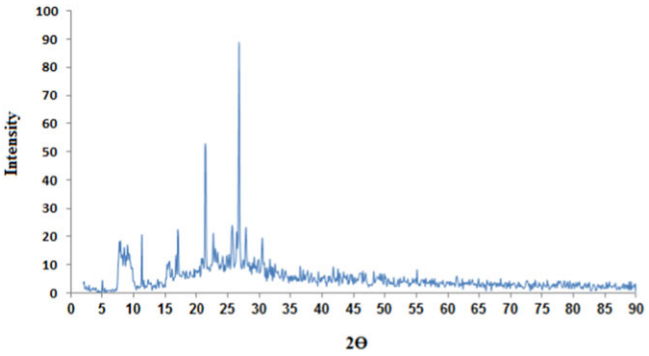
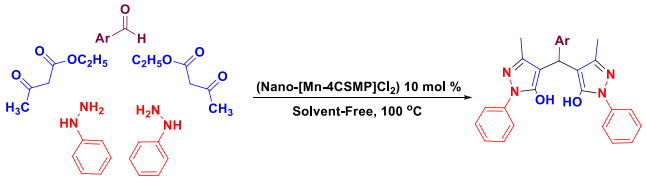


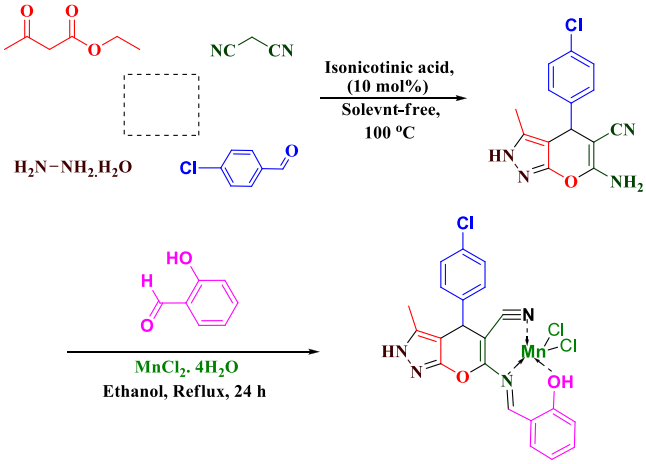
Fig. 2. XRD result of nano-[Mn-4CSMP]Cl_2.



Scheme 1. Preparation of 4,4′-(arylmethylene)-bis (3-methyl-1-phenylpyrazol-5-ol)s using nano-[Mn-4CSMP]Cl_2.

Table 1. XRD data for the catalyst

Entry	2θ	Peak width (FWHM)	Size (nm)	Inter-planar distance (nm)
1	11.3	0.0034	40.90	0.7825
2	17.0	0.0034	41.21	0.5209
3	21.4	0.0043	32.80	0.4148
4	26.8	0.0061	23.35	0.3323



Scheme 2. Preparation of nano-[Mn-4CSMP]Cl_2.

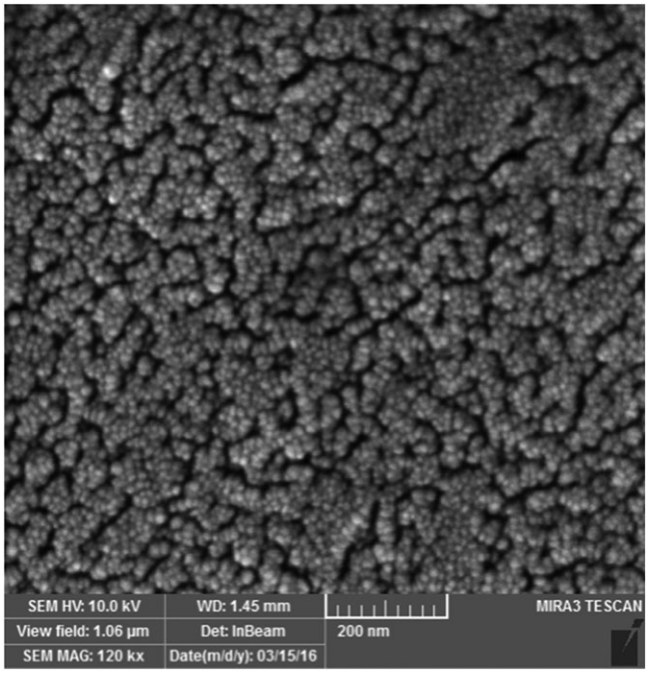


Fig. 3. SEM micrograph of nano-[Mn-4CSMP]Cl_2.

0.3323 nm (λ:Cu radiation 0.154178 nm). The peak width (full width at half-maximum; FWHM), size, and inter-planar spacing of the catalyst are given in Table 1.

SEM micrographs of the catalyst were also studied, which showed that the particles of the catalyst were in the nano-size range, being in good agreement with calculated size through the Debye–Scherrer equation (Figure 3).

EDX spectra of the prepared nanoparticles showed the presence of the expected elements in the structure of nano-[Mn-4CSMP]Cl_2, namely carbon, oxygen, nitrogen, manganese, and chlorine (Figure 4). Therefore, the structure of the catalyst was completely confirmed by EDX analysis.

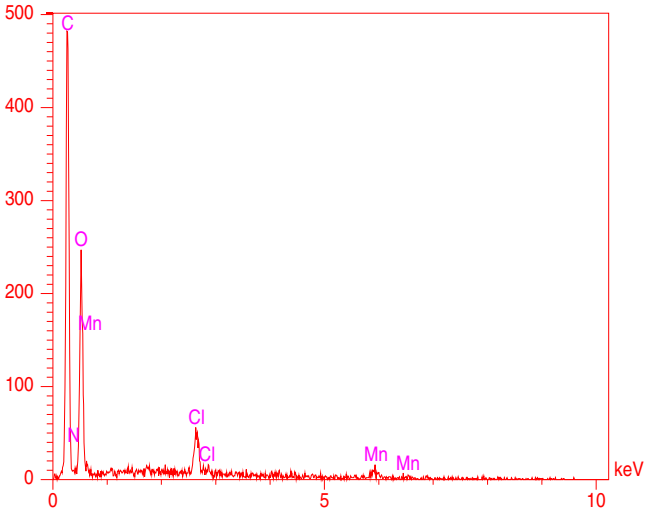


Fig. 4. Energy-dispersive X-ray (EDX) spectrum of nano-[Mn-4CSMP]Cl_2.

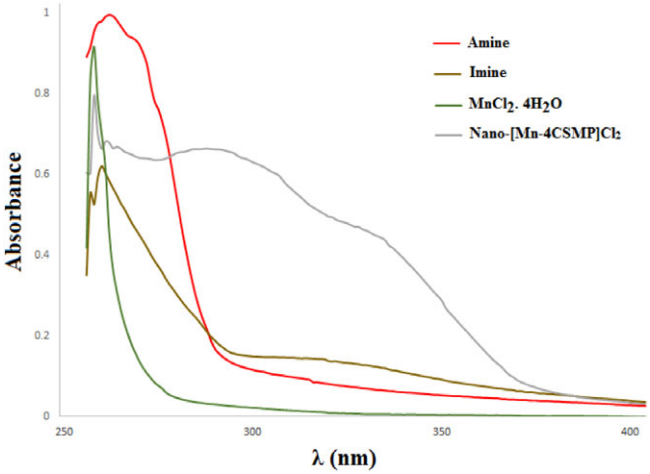


Fig. 6. UV spectra of amine, Schiff base, $MnCl_2.4H_2O$, and nano-[Mn-4CSMP]Cl_2 in DMSO.

TGA of the nano-[Mn-4CSMP]Cl_2 was also carried out. The corresponding results are shown in Figures 5. TG and DTG results of nano-[Mn-4CSMP]Cl_2 showed that it decomposed after 200°C.

The UV spectra also evidenced the production of nano-[Mn-4CSMP]Cl_2. UV studies were carried out in DMSO as solvent. The maximum of absorption for amine, Schiff base (4CSMP), nano-[Mn-4CSMP]Cl_2, and $MnCl_2.4H_2O$ appeared at 263, 261, 257 and 259 nm, respectively (Figure 6). Therefore, λ_{max} of the complex is different from that of the species used for the synthesis of Nano-[Mn-4CSMP]Cl_2.

After full characterization of nano-[Mn-4CSMP]Cl_2, we examined the catalytic activity of the catalyst

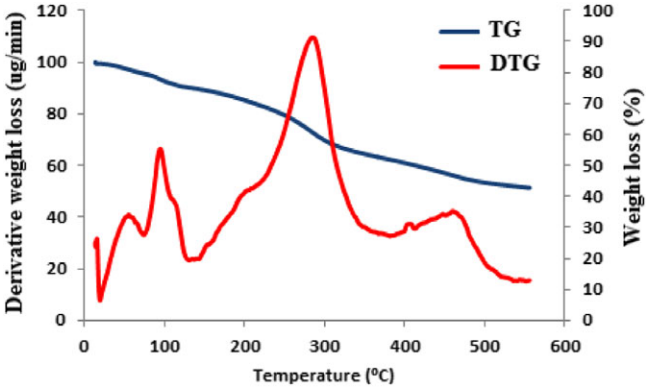


Fig. 5. Thermogravimetric (TG) and differential thermogravimetry (DTG) analysis of nano-[Mn-4CSMP]Cl_2 in the range 0–600°C, at the temperature increase rate of 10°C.

for the preparation of 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s. For this, the reaction of ethyl acetoacetate (2 mmol) and phenyl hydrazine (2 mmol) with 4-chlorobenzaldehyde (1 mmol) was selected as a model reaction and tested in the presence of different quantities of the nano-[Mn-4CSMP]Cl_2 in the temperature range 60–100°C under solvent-free conditions. Higher yield and shorter reaction time were obtained using 10 mol% of catalyst at 100°C under solvent-free conditions.

Then, to explore the efficiency and the scope of the presented protocol, ethyl acetoacetate (2 mmol) and phenyl hydrazine (2 mmol) were treated with various aromatic aldehydes (1 mmol) using nano-[Mn-4CSMP]Cl_2 as catalyst. The corresponding results are summarized in Table 2. As the table shows, all corresponding 4,4′-(arylmethylene)-bis (3-methyl-1-phenylpyrazol-5-ol) derivatives were obtained in good to excellent yields and in relatively short reaction times.

EXPERIMENTAL

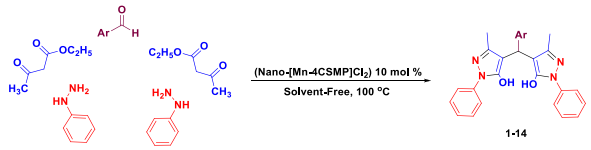
General

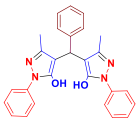
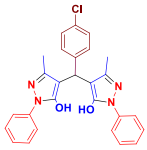
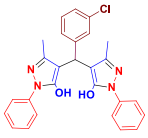
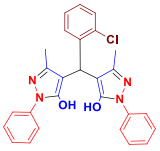
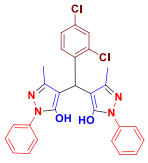
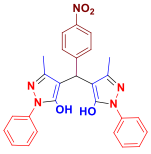
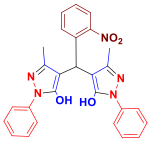
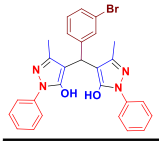
All chemicals were purchased from Merck or Fluka. The known products were identified by comparison of their melting points and spectral data with those reported in the literature.

Procedure for the synthesis of nano-[Mn-4CSMP]Cl_2)

A mixture of 4-chlorobenzaldehyde (1 mmol), malononitrile (0.066 g, 1 mmol), ethyl acetoacetate

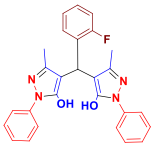
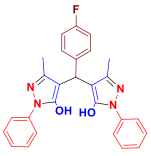
Table 2. Preparation of bis(pyrazolyl)methanes using nano-[Mn-4CSMP]Cl_2

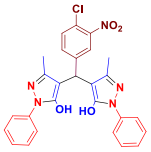
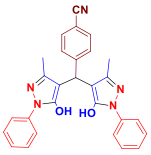
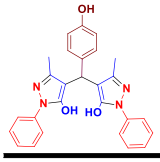


Product	Yield[a]/time (min)	mp. °C (lit.)
	60/45	160–163 (160–162)[5]
	90/30	200–204 (209–210)[5]
	73/60	155–160 (153–154)[5]
	63/50	240–243 (235–236)[5]
	80/80	216–220 (219–221)[5]
	95/30	224–227 (228–230)[5]
	68/60	217–219 (217–218)[5]
	70/20	165–168 (173–175)[18]

(0.13 g, 1 mmol) hydrazine hydrate (1.25 mmol), and isonicotinic acid (0.1 mmol) (0.0123 g, 10 mol%) was taken in a 10-mL round-bottomed flask connected to a reflux condenser and stirred at 85°C. After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature. Water was added to the reaction mixture to dissolve isonicotinic acid, and the aqueous layer was separated from the mixture. Afterwards, the solid residue (crude product) was tritrated by a mixture of ethanol/water (9:1) to afford 6-amino-3-methyl-4-(4-chlorophenyl)-2,4-dihydropyrano [2,3-c]pyrazole-5-carbonitrile as an amine end product.[17] A mixture of the amine (1 mmol) and ethanol (5 mL) was added dropwise to a 25-mL round-bottomed flask containing ethanol (10 mL), salicylaldehyde (1.5 mmol), and $MnCl_2.4H_2O$ (1 mmol) connected to a reflux condenser for 1 h and then stirred for 24 h under reflux conditions. After this time, ethanol was removed and the reaction mixture was washed by ethyl acetate/ hexane (9:1) three times to purify nano-[Mn-4CSMP]Cl_2 from the excess salicylaldehyde.

Table 2. Continued

	65/60	157–159 (157–159)[5]
	93/50	176–180 (175–177)[19]

Ar	Yield[a]/time (min)	mp. °C (lit.)
	83/30	225–228 (232–235)[5]
	85/40	216–220 (214–219)[20]
	59/50	160–163 (151–152)[21]

[a] Isolated yield.

General procedure for the synthesis of bis(pyrazolyl) methanes

A mixture of ethyl acetoacetate (2 mmol), phenyl hydrazine (2 mmol), and nano-[Mn-4CSMP]Cl_2 (10 mol %) was taken in a 10-mL round-bottomed flask connected to a reflux condenser and was stirred at 100°C for 5 min. Then aromatic aldehyde (1 mmol) was added to the reaction mixture and continued stirring for an appropriate time. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and recrystallized from ethanol (95%) The spectra of compounds have been reported in supporting information.

CONCLUSIONS

In summary, we have prepared and characterized nano-[Mn-4CSMP]Cl_2 as a Schiff base complex in nano-size, based on 6-amino-3-methyl-4-(4-chlorophenyl)-2,4-dihydropyrano[2,3-c] pyrazole-5-carbonitrile as a biological compound for the first time. Nano-[Mn-4CSMP]Cl_2 was successfully applied as an efficient and catalyst for tandem cyclocondensation–Knoevenagel–Michael reaction of phenylhydrazine, ethyl acetoacetate arylaldehydes, and malononitrile to give 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s.

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Supporting information

Additional supporting information is available in the online version of this article.

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