

Synthesis of Metal Complexes with Schiff Base for Degradation of Janus Green B Dye

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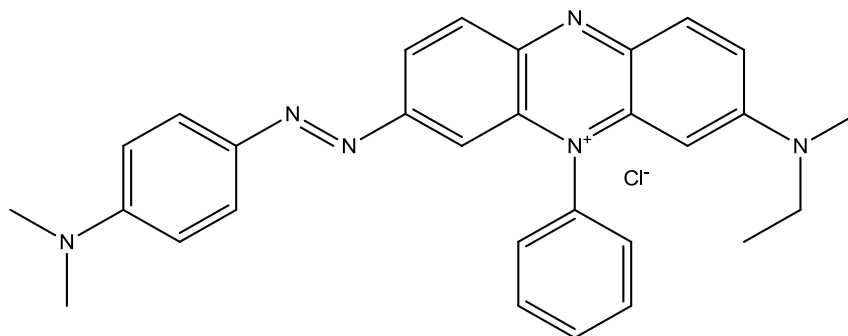
Abstract: A novel series of Pd(II), Pt(II), Hg(II) and Zn(II) complexes have been synthesized from the Schiff base. Structural features were determined by analytical and spectral techniques like IR, ¹H NMR, elemental analysis. The metal complexes were subjected to degradation of Janus Green B dye using prepared metal complexes **6a-d**. The catalytic degradation of Janus green B aqueous solution was investigated using the metal complex **6a-d** as catalysis in presence H₂O₂ by Vis-spectrophotometry. Degradation studies shows among the prepared series of metal complexes **6a-d**, mercury complex **6c** shows maximum degradation of janus green B dye as compared to the other metal complexes.

Key words: Schiff base; Metal complexes; Janus green B; Degradation.

1. Introduction

Contamination of water by point and non point sources has become the leading cause of deaths and diseases worldwide. Water is alleged to be polluted when it unable to support a human use. Many attempts have been made for the treatment of different dyes polluted water using coagulation, adsorption, sedimentation, membrane technology, photocatalytic degradation [1].

Janus Green B (**Figure 1**) is a cationic, basic (which contains both azo and azine chromophore) dye and vital stain used in histology. In 1900, it was introduced by Leonor Michaelis and used to stain mitochondria supravivally. This dye changes color according to the amount of oxygen present [2, 3]. In presence of oxygen the dye is oxidised to blue colour and in absence of oxygen it reduced to pink colour. In serious consideration of the worldwide environmental issues associated with the extensive use of the dyes and effluents generated therefore, the scientists across the world are in search for potential degradation of such dyes has been developed [4].



Dye degradation is a process in which the large dye molecules are broken down chemically into smaller molecules. The resulting products are water, carbon dioxide, and mineral byproducts that give the original dye its color. A significant growing interest in the design of metallic derivatives as drugs and diagnostic agents is currently observed in the area of scientific medicinal inorganic chemistry [5-8]. Schiff base and their metal complexes have been broadly investigated due to

their wide range of applications as catalysts [9]. Many research groups have developed different catalytic methods for different oxidation reaction. Among the various methods, transition metal Schiff base complex catalyzed oxidation reaction is worth mentioning [10, 11]. In the present work, we have studied the degradation of janus green B dye by synthesizing different Schiff base metal complexes.

2. Materials and methods

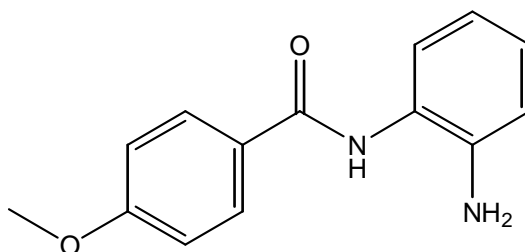
Experimental section

All solvents and reagents were purchased from Sigma Aldrich Chemicals Pvt Ltd. TLC was performed on aluminum-backed silica plates and visualized by UV-light. Melting points (M.P) were determined on an electrically heated VMP-III melting point apparatus. The elemental analysis of the compounds was performed on a Perkin Elmer 2400 elemental analyzer. The results of elemental analyses were within $\pm 0.4\%$ of the theoretical values. The FT-IR spectra were recorded using KBr discs and Nujol on FT-IR Jasco 4100 infrared spectrophotometer. ^1H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer in CDCl_3 and the chemical shifts were recorded in parts per million downfield from tetramethylsilane. Mass spectra were recorded on LC-MS (API-4000) mass spectrometer. MTT was purchased from Sigma Aldrich, USA and CD31 antibodies were procured from Santa Cruz, USA.

Chemistry

A typical procedure is described for the synthesis of N-(2-amino-phenyl)-4-methoxy-benzamide 3a:

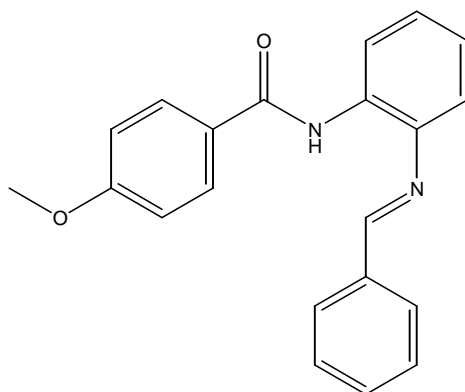
To a solution of p-methoxy benzoic acid **1** (0.0092 mol) in dry dichloromethane (15 mL), o-phenylenediamine **2** (0.0046 mol) were added at 25-30 °C, followed by the addition of lutidine (0.0092 mol). The reaction mixture was stirred at 25-30 °C for 30 min. Then, the reaction was cooled to 0-5 °C, O-(benzotriazol-1-yl)-N,N,N',N''-tetramethyl uronium tetrafluoroborate (TBTU, 0.0138mol) was added over a period of 30 min while maintaining the temperature below 5 °C. The reaction was stirred overnight and monitored by TLC using methanol and chloroform (4:1). The reaction mixture was diluted with 20 mL of DCM and treated with 10% sodium bicarbonate solution (3×20 mL). The organic layer was washed with water (3×25 mL), dried over anhydrous sodium sulfate and concentrated to yield the compound N-(2-amino-phenyl)-4-methoxy-benzamide **3**.



N-(2-amino-phenyl)-4-methoxy-benzamide 3. Yield: 85%. M.P.: 152-155 °C; IR (KBr) ν_{max} (cm^{-1}): 1735 (amide, C=O), 3110-3230 (NH), 3315-3410 (NH_2). ^1H NMR (400 MHz, CDCl_3) δ 3.65 (s, 3H, OCH_3), δ 4.17 (s, 2H, NH_2), δ 6.37-7.83 (m, 8H, Ar-H), δ 9.73 (s, 1H, NH). LC-MS m/z 243 (M+1). Anal. Cal. For $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$ (242): C, 69.41; H, 5.82; N, 11.56. Found: C, 69.36; H, 5.73; N, 11.51%.

A typical procedure is described for the synthesis of N-[2-(benzylidene-amino)-phenyl]-4-methoxy-benzamide 5.

A mixture compound **3** (0.0082 mol) and benzaldehyde **4** (0.0082 mol) in 15 mL of super dry ethanol was stirred overnight with few drops of glacial acetic acid. The completion of reaction was confirmed by TLC and the reaction mixture was then poured into ice cold water and the precipitate obtained was filtered and dried in oven at low temperature. The product was recrystallised from absolute ethanol to afford N-[2-(benzylidene-amino)-phenyl]-4-methoxy-benzamide **5** in a good yield.



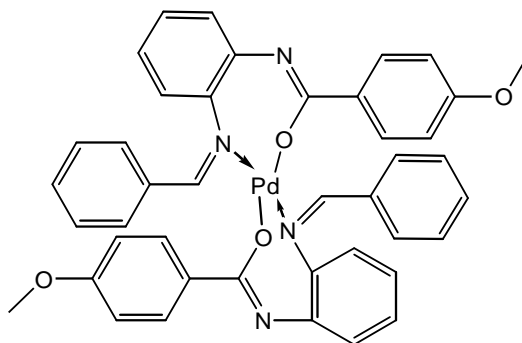
N-[2-(benzylidene-amino)-phenyl]-4-methoxy-benzamide 5. Yield: 90%. M.P.: 138-140 °C; IR (KBr) ν_{\max} (cm⁻¹): 1499 (C=N), 1735 (amide, C=O), 3120-3220 (NH). ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H, OCH₃), δ 6.94-8.66 (m, 13H, Ar-H), δ 9.09 (s, 1H, CH), δ 9.53 (s, 1H, NH). LC-MS m/z 331 (M+1). Anal. Cal. for C₂₁H₁₈N₂O₂ (330): C, 76.34; H, 5.49; N, 8.48. Found: C, 76.23; H, 5.30; N, 8.31%.

General procedure for the synthesis of Metal complex

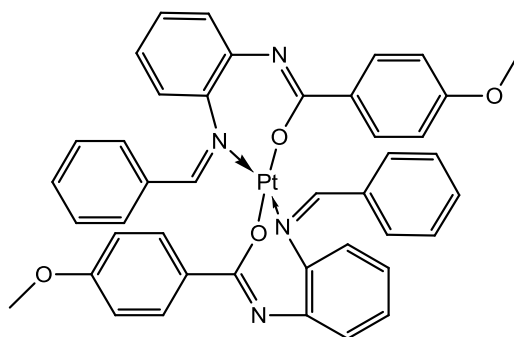
A typical procedure is described for the synthesis of palladium complex.

An aqueous ethanolic solution of Pd(II) chloride (0.0003 mol) was added to the ethanolic solution of the ligand N-[2-(benzylidene-amino)-phenyl]-4-methoxy-benzamide **5** (0.0006 mol) by maintaining 1:2 mol ratio respectively. The mixture was then refluxed with stirring for 5 hours, which resulted in the precipitation of palladium complex **6a**. The final product **6a** formed was filtered, washed and dried in vacuum desiccator.

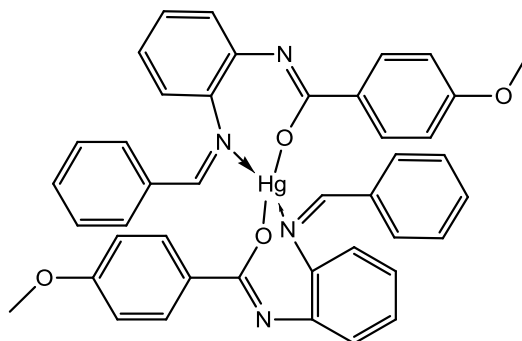
Similarly complexes **6b-d** were synthesized by employing above method.



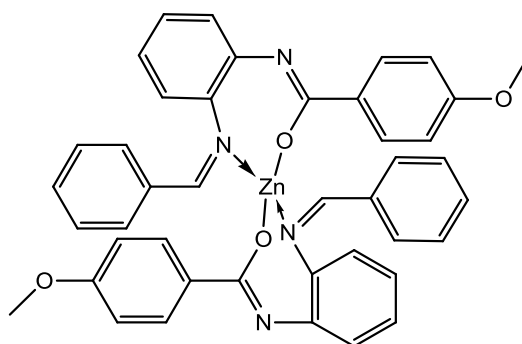
Palladium complex 6a. Yield: 81%. M.P.: 112-114 °C; IR (KBr) ν_{\max} (cm⁻¹): 280 (Pd-O), 435 (Pd-N), 1620 (C=N), 1670 (C=O), 3550-3650 (N-H). ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H, OCH₃), δ 6.94 - 8.66 (m, 13H, Ar-H), δ 9.09 (s, 1H, CH). LC-MS m/z 765 (M+1). Anal. Cal. for C₄₂H₃₄N₄O₄Pd (764): C, 65.93; H, 4.48; N, 7.32. Found: C, 65.82; H, 4.41; N, 7.23%.



Platinum complex 6b. Yield: 75%. M.P.: 119-121 °C; IR (KBr) ν_{\max} (cm⁻¹): 275 (Pt-O), 430 (Pt-N), 1640 (C=N), 1660 (C=O), 3540-3640 (N-H). ¹H NMR (400 MHz, CDCl₃) δ 3.65 (s, 3H, OCH₃), δ 6.81 - 8.77 (m, 13H, Ar-H), δ 8.89 (s, 1H, CH). LC-MS m/z 855 (M+1). Anal. Cal. for C₄₂H₃₄N₄O₄Pt (854): C, 59.08; H, 4.01; N, 6.56. Found: C, 59.03; H, 3.98; N, 6.45%.



Mercury complex 6c. Yield: 79%. M.P.: 121-123 °C; IR (KBr) ν_{\max} (cm⁻¹): 260 (Hg-O), 440 (Hg-N), 1610 (C=N), 1650 (C=O), 3450-3550 (N-H). ¹H NMR (400 MHz, CDCl₃) δ 3.53 (s, 3H, OCH₃), δ 6.84 - 8.73 (m, 13H, Ar-H), δ 9.12 (s, 1H, CH). LC-MS m/z 861 (M+1). Anal. Cal. for C₄₂H₃₄HgN₄O₄Hg (860): C, 58.70; H, 3.99; N, 6.52. Found: C, 58.61; H, 3.87; N, 6.45%.



Zinc complex 6d. Yield: 81%. M.P.: 112-114 °C; IR (KBr) ν_{\max} (cm⁻¹): 280 (Zn-O), 435 (Zn-N), 1620 (C=N), 1670 (C=O), 3550-3650 (N-H). ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H, OCH₃), δ 6.94 - 8.66 (m, 13H, Ar-H), δ 9.09 (s, 1H, CH). LC-MS m/z 725 (M+1). Anal. Cal. for C₄₂H₃₄N₄O₄Zn (724): C, 65.93; H, 4.48; N, 7.32. Found: C, 65.82; H, 4.41; N, 7.23%.

4. Results and discussion

The synthesis of the title complex **6a-d** was accomplished by a synthetic procedure as shown and discussed in material and methods (**Scheme 1**). All the synthesized compounds were established by IR, NMR, and mass spectral data.

The compound **3** confirmed by the disappearance of COOH and NH₂ stretching bands of the compound **1** and **2** respectively, and the appearance of only NH stretching between the range of 3100-3210 cm⁻¹ in the IR spectra. It was also proved by the proton NMR spectrum by the disappearance of COOH proton of compound **1** and NH₂ proton of compound **2** and the appearance of singlet peak of NH proton at δ 9.09 ppm, besides there is an increase in aromatic protons in a coupled product **3** in the range δ 6.94-8.66 ppm. The mass spectrum of compound **3** exhibited M+1 peak at m/z 242 which also revealed the formation of the compound **3**.

The IR spectrum of the compound **5** was confirmed by the disappearance of NH₂ stretching of the compound **3** and the appearance 1499 cm⁻¹ (C=N), 1735 cm⁻¹ (amide, C=O), 3120-3220 cm⁻¹ (NH) absorption peak. In addition, ¹H NMR spectrum showed disappearance of NH₂ proton of the compound **3** and the appearance of N=CH protons at δ 9.53 ppm, besides there is an increase in aromatic protons in a coupled product **5** in the range δ 6.94-8.66 ppm. The mass spectrum of compound **5** exhibited M+1 peak at m/z 331 which also revealed the formation of the compound **5**. Finally, in the title synthesized series **6a-d**, compound **6a** is taken as a representative example to explain characterizations of this series. The IR spectrum showed bands in the region of 420-450 cm⁻¹ corresponding to (Pd-N) vibrations. The presence of these bands supports the fact concerning the coordination of the azomethine nitrogen with the metal. The bands present at 510-540 cm⁻¹ in complex were due to (Pd-O) also affirmed the formation of palladium complex.

Investigation of Janus green degradation of the Schiff's base of metal complexes 6a-d

The complexes **6a-d** (0.001 mol) and H₂O₂ (1.0 mL, 30%, 10 mmol) were added into the Janus green dye solution (0.023 g/L, 500 mL, 0.02 mmol) and stirred at room temperature. The transmittance (T) of the mixture was determined by Vis-spectra (λ=660 nm) method. The graphs were plotted transmittance verses time curve (**Figure 2**) and rate verses time (**Figure 3**). The plot indicates that the degradation studies of different metal complexes on Janus green B dye (**Table 1**).

Further, the UV-visible spectrophotometer is often very useful in the evaluation of results furnished by other methods of structural investigation. The transmittance data in **Table 1** recorded from UV-visible spectrophotometer and hence calculated absorbance and rate of the degradation which show that the catalytic activity of metal complexes in the degradation of janus green B. The mercury complex **6c** showed the good degradation of janus green B dye (**Figure 1 and 2**).

$$\text{Rate (\%)} = [(OD_0 - OD_t) / OD_0] \times 100$$

(OD₀ is the value at t=0 min, OD_t is the value at t min)

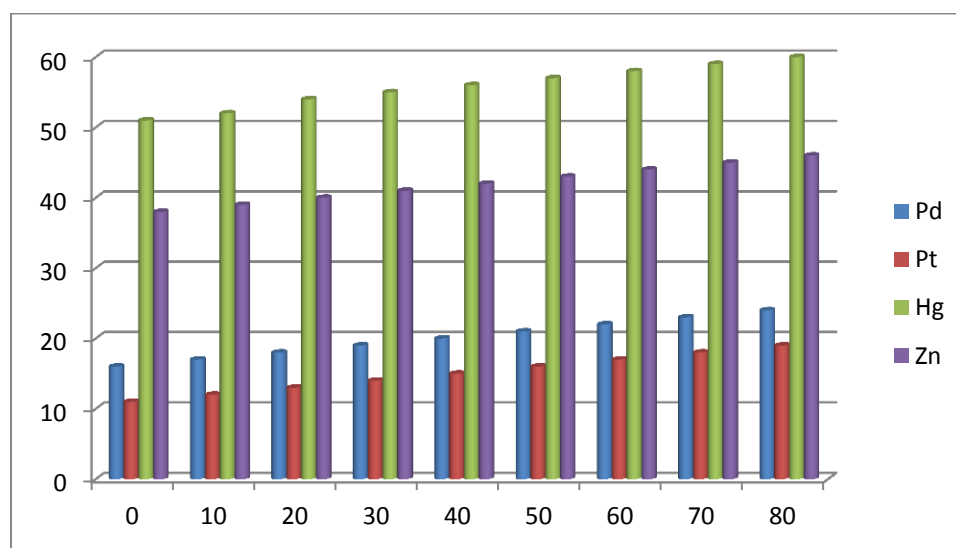


Figure 2: The decolorization (degradation) rate of janus green to time curve v/s transmittance

Table 1: A typical run of degradation of Janus green B by different metal complexes

Time		0	10	20	30	40	50	60	70	80
Absorbance	Pd	0.795	0.769	0.744	0.721	0.698	0.677	0.657	0.638	0.619
	Pt	0.958	0.920	0.886	0.853	0.823	0.795	0.769	0.744	0.721
	Hg	0.292	0.283	0.267	0.259	0.251	0.244	0.236	0.229	0.221
	Zn	0.42	0.408	0.397	0.387	0.376	0.366	0.356	0.346	0.337
Transmittance	Pd	16	17	18	19	20	21	22	23	24
	Pt	11	12	13	14	15	16	17	18	19
	Hg	51	52	54	55	56	57	58	59	60
	Zn	38	39	40	41	42	43	44	45	46
Rate	Pd	0	3.270	6.415	9.308	12.20	14.842	17.35	19.748	22.138
	Pt	0	3.966	7.515	10.96	14.091	17.014	19.728	22.338	24.739
	Hg	0	3.082	8.561	11.301	14.041	16.438	19.178	21.575	24.315
	Zn	0	2.857	5.476	7.857	10.476	12.857	15.238	17.619	19.761

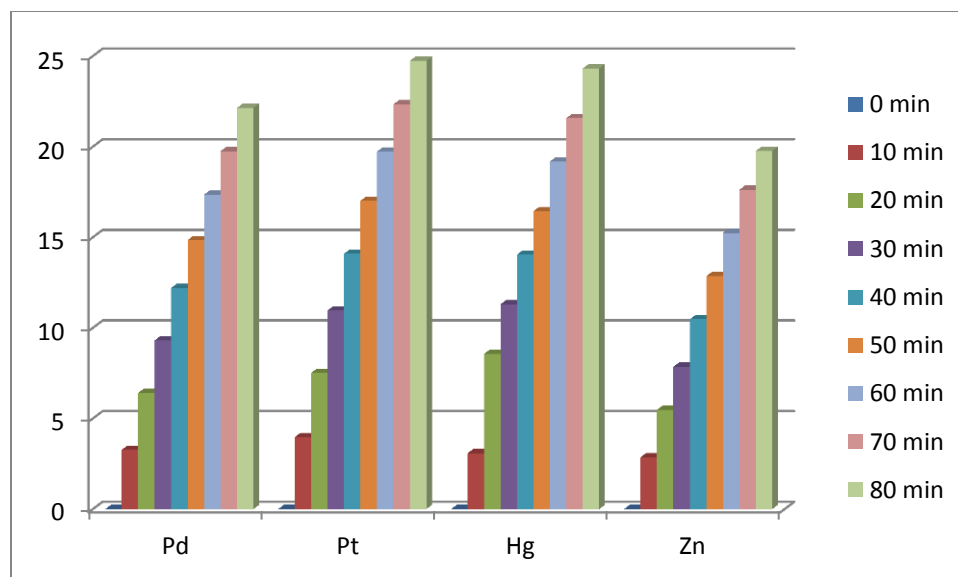


Figure 3: The decolorization rate of Janus green B dye to time curve v/s rate

Conclusion

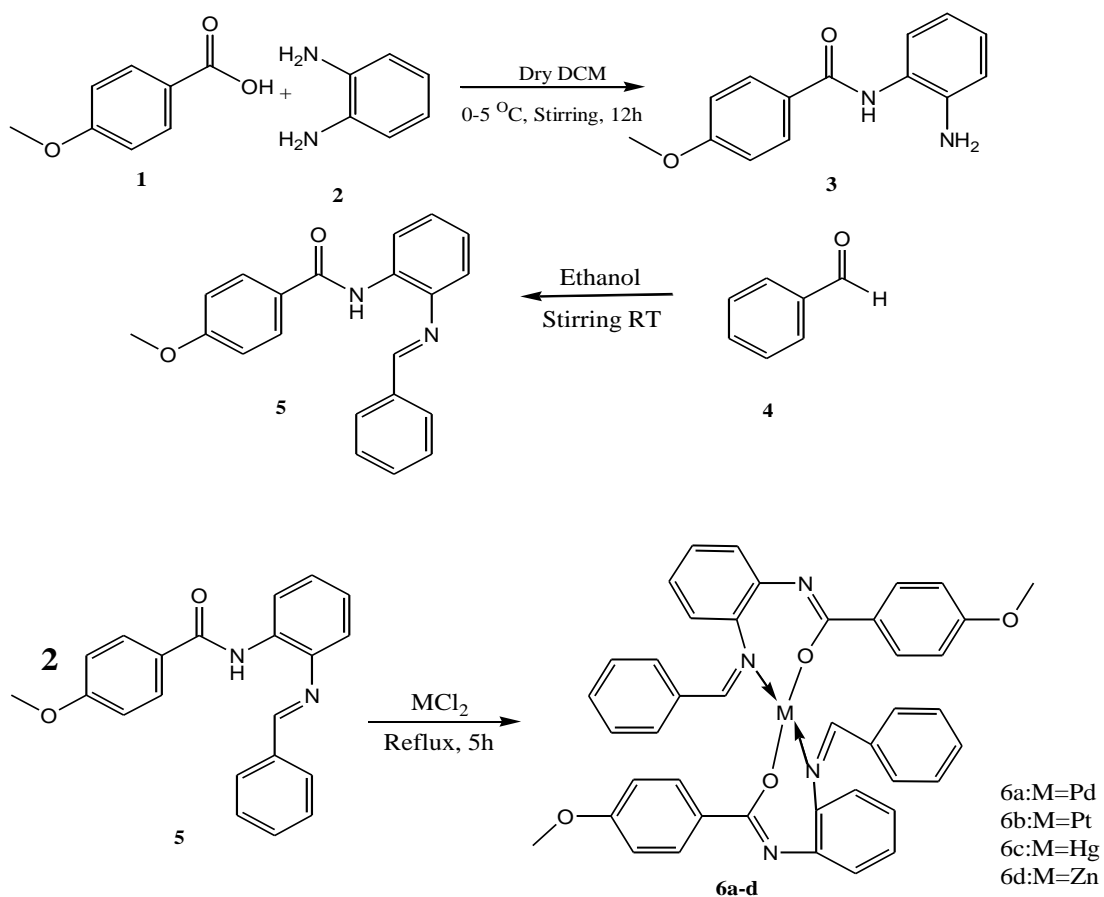
The coordination reaction of the Schiff base ligand with different MCl_2 a novel metal complex with the Schiff base ligand was prepared and characterized by IR spectra and elemental analysis. The catalytic degradation of Janus green B aqueous solution was investigated using the metal complex as catalysis in presence H_2O_2 by Vis-spectrophotometry. The result of characterization showed that there are four coordination sites around M (II) in complex, which are respectively occupied by two nitrogen atom (from the two Schiff base ligands), two oxygen atom (from the two Schiff base ligand). The degradation of Janus green B indicated that the complex show the properties of enzyme activity. Also, degradation studies shows that type of metal is also play a important role in degradation of janus green B dyes. The result found that, among the synthesis series of metal complexes **6a-d**, mercury complex **6c** shows highest degradation of janus green B dye as compared to the other metal complexes. Further, the plan is focused onto report on degradation studied of different dyes using more modified mercury complex **6c** in near future.

Acknowledgements

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References

- [1]. S. Jakar, R.Chaturvedi, M. K. Sharma, Int. J. Chem. Sci., 12(2), 2014, 573.
- [2]. J. C. Hindson, B. Ulgut, R. H. Friend, N. C. Greenham, B. Norder, A. Kotlewskic, T. J. Dingemans, J. Mater. Chem., 20, 2010, 937.
- [3]. M. L. Petrus, T. Bein, T. J. Dingemans, P. Docampo. J. Mater. Chem., 3, 2015, 12159.
- [4]. S. Braun, M. Erdelyi, A. Udvardy, Cancer Research, 27, 1967, 660.
- [5]. K. H. Thompson, C. J. Orvig, Chem. Soc., Dalton Trans., 2006, 761
- [6]. A. R. Timerbaev, C. G.Hartinger, S. S. Aleksenko, B. K. Keppler, Chem. Rev., 106, 2006, 2224.
- [7]. L. J. Ming, Med. Res. Rev., 23, 2003, 697.
- [8]. A. Y. Louie, T. J. Meade, Chem. Rev., 99, 1999, 2734
- [9]. K. C. Gupta, A. K. Sutar, Coord. Chem. Rev., 252, 2008, 1420.
- [10]. I. Fernandez, J. R.Pedro, A. L.Rosello, R. Ruiz, I.Castro, X. Ottenwaelder, Y. Journaux, Eur. J. Org. Chem., 2001, 1235.
- [11]. A.B. Begum, N.D. Rekha, B.C. V. Kumar, V. L. Ranganatha, S. A. Khanum, Bioorg. & Med. Chem. Let, 24 (15), 2014, 3559.



Scheme 1