

SYNTHESIS AND CHARACTERIZATION OF NI(II), Pd(II) and Cu(II) COMPLEXES OF SCHIFF BASE DERIVED FROM AMINO-1,2,3,6-OXATRIAZINE AND SALICYLADEHYDE

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Abstract: Schiff base **5** was prepared by condensation reaction of salicylaldehyde with 4-amino-2-(4-chlorophenyl)-5-methyl-2H-1,2,3,6-oxatriazine **3** in refluxing ethanol.

Square planar complexes of Ni(II), Pd(II) and Cu(II) **6a-c** of Schiff base **5** were obtained from their reaction with $M(OAc)_2$ in a 2:1 mol ratio in refluxing ethanol for 4 hours. The new compounds (**5**, **6a-c**) were characterized by elemental analysis, IR, 1H NMR, ^{13}C NMR, MS and HRMS spectra.

Key words: 1,2,3,6-oxatriazine, salicylaldehyde, Schiff base, Nickel, Palladium, Copper.

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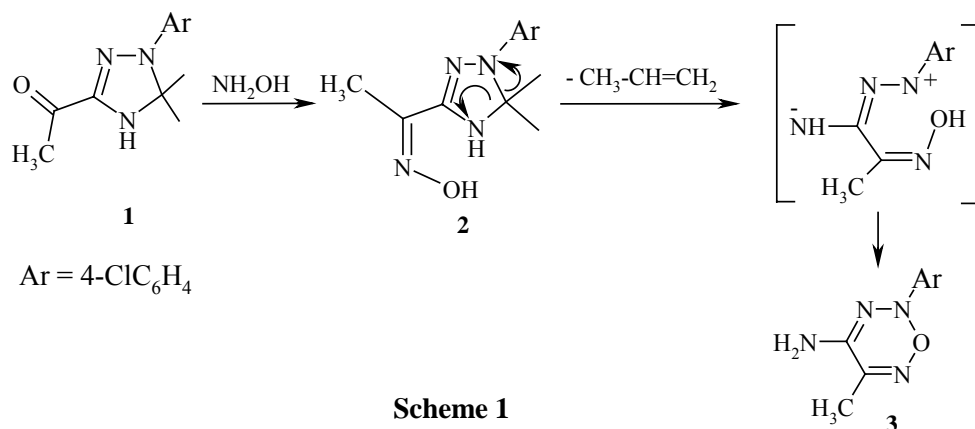
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Introduction

Schiff bases have been widely used as bidentate ligands in the field of coordination chemistry [1-5]. The Schiff base complexes have been used in catalytic reactions [6] and as models for biological systems [7, 8]. In recent years many Copper complexes of Schiff bases were prepared [9-14]. It has been reported that the structure of the substituent bonded to the imino nitrogen affects the coordination geometry of the complex [15].

Quite recently, we prepared the novel heterocyclic system 4-amino-2-(4-chlorophenyl)-5-methyl-2H-1,2,3,6-oxatriazine **3** via ring transformation of the triazole oxime(**2**) prepared from the corresponding triazole **1**(Scheme 1).

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In this work, we will investigate the chemistry of this novel heterocyclic compound by preparing its Schiff base with salicylaldehyde, and study the complexation behavior of the new Schiff base with some transition metals.

Results and Discussion

Compound **3** was prepared by refluxing the triazole **1** with with hydroxylamine hydrochloride in presence of sodium acetate in ethanol/water mixture for 5 hours according to standard procedure.

Schiff base **5** was readily accessible via condensation reaction of 4-amino-1,2,3,6-oxatriazine **3** with small excess of salicylaldehyde **4** in refluxing ethanol.

Satisfactory elemental analysis, IR, ^1H NMR, ^{13}C NMR, MS and HRMS spectra were obtained for this compound.

Refluxing the Schiff base **5** with metal acetates of Ni(II), Pd(II) and Cu(II) in ethanol for 4 hours led to the formation of the complexes **6a-c**.

Structural assignment of the formed complexes **6** was based on satisfactory spectral and electronic data.

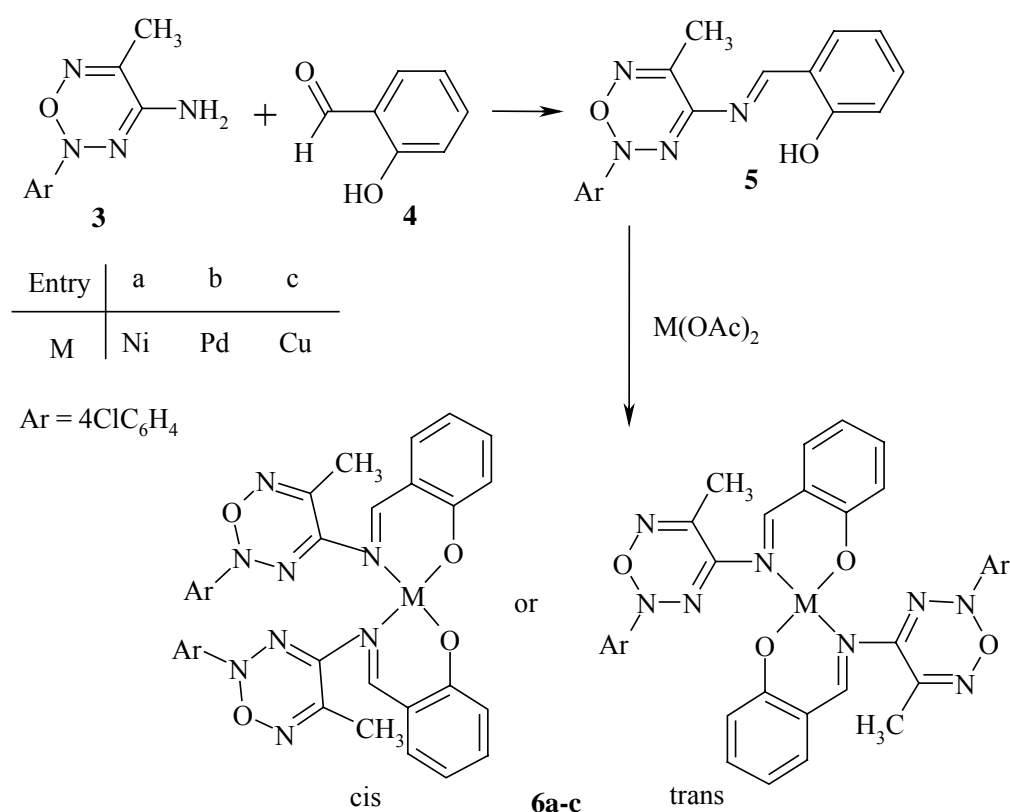
Electron impact mass spectra gave the correct molecular ions in accordance with the suggested structures.

The absence of the OH signal both in the IR and ^1H NMR suggests that coordination occurs through both the oxygen atom and the imino nitrogen atom of the Schiff base.

^{13}C NMR spectra gave the correct number of carbon signals required by the suggested structures.

The electronic spectrum of the Ni(II) complex **6a** shows two bands at 18450 cm^{-1} and 13500 cm^{-1} which are attributed to $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{B}_{2g}$ transitions [16]. These transitions suggest a square-planar stereochemistry of the compound. The electronic spectrum of the Pd(II) complex **6b** display

two absorption bands around 24690 assigned to ${}^1A_{1g} \rightarrow {}^1E_{2g}$ transition, and 17540 cm^{-1} that are assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which are consistent with square planar Pd(II) complex [17], and the electronic spectrum of Cu(II) complex **6c** exhibits bands at 21400 cm^{-1} and 15500 cm^{-1} which can be assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transitions, these transitions suggest also a square planar Cu(II) complex [18, 19].



Scheme 2

X-Ray-structure determination of similar copper complexes carrying planner substituents at the imino nitrogen atom revealed a cis coordination geometry for the complexes [15].

Experimental

Melting points (uncorrected) were determined on an electrothermal Mel. Temp. apparatus. IR spectra were obtained by using Perkin-Elmer 237 infrared spectrometer (KBr discs) ${}^1\text{H}$ - and ${}^{13}\text{C}$ nmr spectra were recorded on a Bruker 300 MHz instrument for solution in CDCl₃ at 21°C, using TMS as

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an internal reference. Chemical shifts are expressed in δ (ppm) downfield from TMS. Electron impact ms were run on Finnigan Mat 8200 and 8400 series double focusing sector field spectrometer at 70 eV. 1,2,3,6-Oxatriazine **3** was prepared by Refluxing 1,2,4-triazole **1** with hydroxylamine hydrochloride and sodium acetate in ethanol for 5 hours [20].

Synthesis of 2-(4-chlorophenyl)-5-methyl-4-salicyladimin-2H-1,2,3,6-oxatriazine (5)

To a solution of the oxatriazine **3** (0.5 g, 2.2 mmol) in ethanol (25 mL) was added salicylaldehyde (0.3 g, 2.5 mmol) in ethanol (25 mL). The resulting reaction mixture was refluxed for 3 hours. The solvent was then concentrated to 25 mL and the product was separated and washed with petroleum ether (40-60 °C). Yield (0.6 g, 82 %), mp 165-166 °C; ir: 3496 (OH), 1626, 1611 cm^{-1} (C=N); ^1H nmr: δ 12.4 (s, 1H, OH), 9.2 (s, 1H, C-H), 6.9-7.9 (m, 8H, aromatic protons), 2.4 (s, 3H, CH_3); ^{13}C nmr: 165.1 (CH=N), 161.6, 147.7 (2 C=N), 134.8, 134.6, 133.7, 133.5, 129.4, 123.8, 121.4, 119.8, 118.6, 117.6 (10 signals for the aromatic carbons), 24 (CH_3); ms: m/z 328/330 (M^+); hrms (M. Wt = found 328.072794, calcd. 328.072703, mass difference for $\text{C}_{16}\text{H}_{13}\text{ClN}_4\text{O}_2 = -0.28$).

Synthesis of bis[2-(4-chlorophenyl)-5-methyl-4-salicyladimin-2H-1,2,3,6-oxatriazine] metal(II) (6a-c):

To a solution of the Schiff base **5** (0.6 mmol) in absolute ethanol (25 mL) was added a solution of metal acetate (0.3 mmol) in ethanol (25 mL). The resulting reaction mixture was refluxed for 4 hours, refrigerated for 2 hours. The solid product formed was collected by suction filtration, washed with cold ethanol (5 mL) and then with petroleum ether (40-60 °C).

The following complexes were prepared using this method:

bis[2-(4-chlorophenyl)-5-methyl-4-salicyladimin-2H-1,2,3,6-oxatriazine] nickel(II) (6a):

From 0.2 g (0.6 mmol) of **5**: yield 0.07 g (32 %) dark green yellow, mp 270-272 °C; ir: 1609, 1589 (C=N) cm^{-1} ; ^1H nmr: δ 9.2 (s, C-H), 7.2-8.0 (aromatic protons), 2.4 (s, 3H, CH_3); ^{13}C nmr: 165.2 (CH=N), 161.6, 147.0 (2 C=N), 134.8, 134.6, 133.7, 133.4, 129.4, 123.8, 121.4, 119.8, 118.6, 117.6 (aromatic carbons), 7.4 (CH_3); ms: m/z 712/714/716 (M^+).

bis[2-(4-chlorophenyl)-5-methyl-4-salicyladimin-2H-1,2,3,6-oxatriazine] palladium(II) (6b):

From 0.2 g (0.6 mmol) of **5**: yield 0.16 g (88 %) dark tan, mp > 300 °C; ir: 1605, 1589 (C=N) cm^{-1} ; ^1H nmr: δ 8.0 (s, C-H), 7.1-7.9 (aromatic protons), 2.4 (s, 3H, CH_3); ^{13}C nmr: 165.4 (CH=N), 165.9, 148.7 (2 C=N), 137.8,

135.6, 134.6, 133.7, 129.4, 123.7, 122.5, 121.2, 119.4, 116.6 (aromatic carbons), 8.3 (CH₃); ms: m/z 760/762/764 (M⁺).

bis[2-(4-chlorophenyl)-5-methyl-4-salicyladimin-2H-1,2,3,6-oxatriazine] copper(II) (6c):

From 0.2 g (0.6 mmol) of **5**: yield 0.21 g (91 %) dark tan, mp 245 °C; ir: 1608, 1584 (C=N) cm⁻¹; ms: m/z 717/719/721 (M⁺); the compound is insoluble in NMR solvents.

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