Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 75 (2007) 294–297

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

# Rapid, efficient and facile synthesis and characterization of novel Schiff bases and their complexes with transition metal ions

Hossein Naeimi*, Khadigeh Rabiei, Fariba Salimi

*Chemistry Department, Faculty of Sciences, Kashan University, Kashan 87317, Islamic Republic of Iran*

Received 10 May 2006; accepted 6 June 2006
Available online 22 August 2006

## Abstract

Novel complexes of Co(II), $UO_2$(II) and Cu(II) ions with new Schiff bases derived from salicylaldehyde, ammonium benzoate and aromatic aldehydes in the presence of triethylamine via one pot three component reaction have been synthesized and characterized by several techniques using elemental analyses (CHN), infrared, mass spectroscopy, $^1$H NMR, $^{13}$C NMR and UV–vis spectra.

*Keywords:* Schiff base; Three component; Complex; Aromatic aldehydes

## 1. Introduction

The development of the so-called Schiff base compounds has attracted a lot of interest in the fields of coordination chemistry and material sciences [1,2]. Schiff bases that have solvent dependent UV–vis spectra (solvatochromicity) can be suitable NLO (non linear optical active) materials [3].

The presence of ion pair on the nitrogen atom of the imino group enables the coordination of numerous metal cations [4]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [5] because of their ability to possess unusual configuration, being structurally labile and their sensitivity to molecular environments [6]. Schiff base can accommodate different metal centers involving various coordination modes thereby allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry [7]. This feature is employed for modeling active sites in biological systems [8,9]. Additionally, they have wide applications such as antibacterial and antifungal agents [10]. These compounds also find many important catalytic applications, ranging from asymmetric epoxidation [11], Lewis acid assisted organic transformations [12], solid phase extraction of metal ions [13] to various types of polymerization [14–17] as well as their application for the preparation of ion selective electrodes [18–22].

In attention to importance of these compounds many literatures have been published in this field. In view of this, recently, multicomponent reaction has much attention and many of them have been reported.

First, we describe the successful synthesis of novel Schiff bases through one pot three component reaction using salicylaldehyde, ammonium benzoate and aromatic aldehydes in the presence of $NEt_3$ under solvent free conditions.

In continuation of our research on the synthesis of Schiff bases and their complexes of metal ions [23–25], we have studied the preparation of complexes of these Schiff bases with transition metal ions under mild conditions. The corresponding complexes were characterized by spectroscopic and physical data.

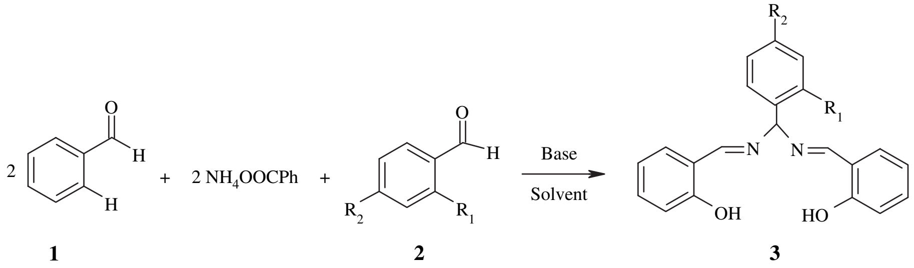
## 2. Results and discussion

Four Schiff base ligands, *N*,*N*′-bis(2-hydroxybenzilidene)-arylmethanediamine have been prepared from salicylaldehyde, ammonium benzoate and aromatic aldehydes in the presence of triethylamine under solvent free conditions (Scheme 1).

---

* Corresponding author. Tel.: +98 361 5555333; fax: +98 361 5552935.
*E-mail address:* naeimi@kashanu.ac.ir (H. Naeimi).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.06.001



| | $R_1$ | $R_2$ |
|---|---|---|
| **3a** | H | H |
| **3b** | OMe | H |
| **3c** | H | $NO_2$ |
| **3d** | OH | H |

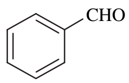
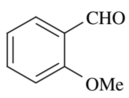
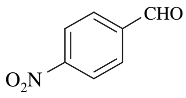
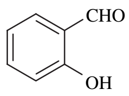
Scheme 1. Preparation of Schiff bases from salicylaldehyde.

As shown in Scheme 1, when 2 mol of salicylaldehyde, 2 mol ammonium benzoate and 1 mol aromatic aldehyde were allowed to react together under free solvent condition, and the corresponding products (**3**) were characterized by spectroscopic and physical data. In the domain of material science, the main advantage in the use of Schiff base ligands relates to the availability of a free imino site that can be functionalized with a wide variety of appendages.

The results of these reactions are shown in Table 1. As indicated in this table, a lot of useful double Schiff bases were afforded in high yields and short reaction times from the one pot reaction of various aromatic aldehydes with salicylaldehyde and ammonium benzoate.

In continuation of our investigation on the preparation of Schiff base complexes, we have synthesized Schiff base complexes by treating the above mentioned Schiff base ligands with transition metal ions such as $UO_2^{2+}$, $Co^{2+}$, $Cu^{2+}$, at room temperature and mild reaction conditions. The reaction of Schiff base ligands with the corresponding metal salts may be represented in Scheme 2.

Table 1
The obtained results related to the synthesis of Schiff bases

| Entry | Substrate | Product | Time (h) | mp (°C) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 |  | **3a** | 2 | 118–120 | 95 |
| 2 |  | **3b** | 1 | 145–147 | 98 |
| 3 |  | **3c** | 0.7 | 116–118 | 95 |
| 4 |  | **3d** | 1.5 | 164–166 | 90 |

[a] Isolated products' yields based on salicylaldehyde.

As shown in Scheme 2 when 1 mol of ligand reacts with 1 mol transition metal salt, the complex products can be prepared in methanol solution under mild conditions at room temperature. The results of these reactions are summarized in Table 2. As can be seen in this table, four Schiff base complexes of metal (II) were afforded in excellent yields and short reaction times from the reaction of ligands with the transition metal salts. Most of the synthesized complexes are colored and are stable in air, soluble in DMSO, DMF, MeOH and EtOH but poorly soluble in diethyl ether.

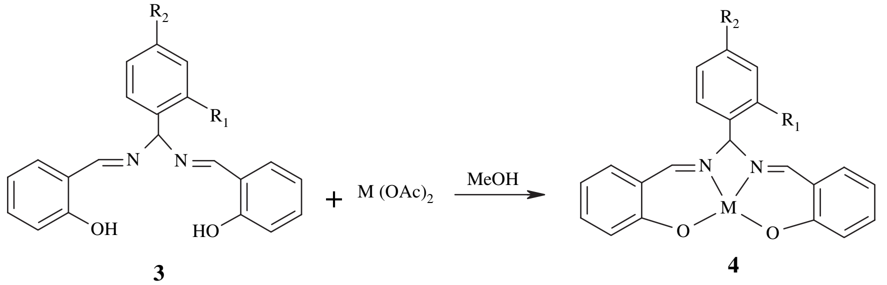
The infrared spectrum of the Schiff base exhibits a band at 1625 $cm^{-1}$ assignable to $\nu$ (C=N) of azomethine. This band shifts to lower region by about 10–15 $cm^{-1}$ on chelation of ligand with the metal ion. The band of OH group in the free ligands, the broad signal around $\delta = 12.5$–$13.1$ ppm are assigned to the protons of the hydroxyl groups. Two protons of CH=N have the same chemical shifts in the range of $\delta = 8.5$–$8.9$ ppm. The signal around $\delta = 6.0$–$6.65$ ppm is assigned to the protons of the NCHN and signals around $\delta = 6.6$–$7.90$ ppm are assigned to the protons of aromatic rings (CH=CH). In the $^1H$ NMR spectra of the Schiff base complexes, all these signals shift to lower field about 0.6 ppm and the broad signals around $\delta = 12.5$–$13.1$ ppm are disappeared.

In conclusion, we have reported a mild, easy, clean and a very efficient method for the synthesis of some novel Schiff base complexes of metal (II) without reflux conditions at room temperature. Also the desired Schiff bases for the preparation of these complexes have been obtained through easy, simple, three component reaction of salicylaldehyde with aromatic aldehydes and ammonium benzoate in methanol solution. The products are obtained in excellent yields and with short reaction times.

## 3. Experimental

### 3.1. Materials

All the materials were of commercial reagent grade. The salicylaldehyde and other aldehyde compounds were purified by



Scheme 2. Synthesis of Schiff base complexes of metal (II).

standard procedures. The purity of them was determined by thin layer chromatography (TLC) and gas chromatography (GC).

### 3.2. Apparatus

IR spectra were recorded as KBr pellet on a Perkin–Elmer 781 Spectrophotometer and an Impact 400 Nicolet FTIR Spectrophotometer. $^1H$ NMR spectra were recorded in DMSO on a (400 MHz) Spectrometer using TMS as an internal reference. Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. The purity determination of the substrates and reactions monitoring was accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

### 3.3. General procedure

#### 3.3.1. General procedure for the synthesis of N,N′-bis-(salicylidene)-arylmethanediamines

To a solution of salicylaldehyde (0.38 g, 3 mmol) and benzaldehyde (0.16 g, 1.5 mmol) in methanol (5 ml) was added $NH_4O_2CPh$ (0.25 g, 3.27 mmol) in the presence of the $NEt_3$ (0.6 ml) as a base by stirring in one portion. Stirring of the mixture is continued for 2 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, pale yellow substance was obtained. The solid product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base, *N,N′*-bis(salicylidene)-phenylmethane-diamine was obtained in 95% yield, mp = 118–120 °C. The Schiff base products were identified by physical and spectroscopic data.

*3.3.1.1. N,N′-Bis(salicylidene)-phenylmethanediamine (**3a**).* Pale yellow solid; mp 118–120 °C; IR (KBr)/$\nu$ (cm$^{-1}$) 3300–3500 (br, OH), 1625 (s, C=N), 1450, 1550 (Ar); $^1H$ NMR/DMSO/$\delta$ (ppm): 6.1 (s, 1H, NCHN), 6.63–7.35 (m, 13H), 8.6 (s, 2H, HC=N), 12.80 (s, 2OH); $^{13}C$ NMR/DMSO/$\delta$ (ppm): 90, 118, 119, 119.5, 127.5, 130.1, 130.3, 138, 161, 167; UV ($CHCl_3$)/$\lambda_{max}$ (nm) 320 (w), 260 (s); MS: $m/z = 331$ ($M^+ + 1$, 3), 330 ($M^+$, 9), 210 (60), 209 (80), 91 (70), 89 (100), 77 (50); Anal. Calcd. for C, H, N: 76.36 (C), 5.45 (H), 8.48 (N); found: 76.36 (C), 5.46 (H), 8.49 (N).

Table 2
The results regarding the reactions for the preparation of Schiff base complexes

| Entry | Substrate | $M^{2+}$ | Product | Time (h) | mp (°C) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | **3a** | Co | **4a** | 2 | >300 | 95 |
| 2 | **3b** | $UO_2$ | **4b** | 1 | >300 | 98 |
| 3 | **3c** | Cu | **4c** | 0.7 | >300 | 95 |
| 4 | **3d** | $UO_2$ | **4d** | 1.5 | 198–200 | 90 |

[a] Isolated yields.

*3.3.1.2. N,N′-Bis(salicylidene)-2-methoxy-phenylmethanediamine (**3b**).* Yellow solid; mp 145–147 °C; IR (KBr)/$\nu$ (cm$^{-1}$) 3375–3625 (br, OH), 1625 (s, C=N), 1450, 1510 (Ar); $^1H$ NMR/DMSO/$\delta$ (ppm): 2.3 (3H, $OCH_3$), 6.2 (s, 1H, NCHN), 6.7–7.4 (m, 12H), 8.6 (s, 2H, HC=N), 12.90 (s, 2OH); $^{13}C$ NMR/DMSO/$\delta$ (ppm): 60, 90, 117, 119, 119.2, 129.5, 130.2, 130.3, 138, 165, 170; UV ($CHCl_3$)/$\lambda_{max}$ (nm) 324 (w), 262 (s); MS: $m/z = 361$ ($M^+ + 1$, 2), 360 ($M^+$, 6), 241 (50), 240 (80), 120 (70), 119 (100), 77 (15); Anal. Calcd. for C, H, N: 73.3 (C), 5.5 (H), 7.8 (N); found: 72.69 (C), 5.48 (H), 8.07 (N).

*3.3.1.3. N,N′-Bis(salicylidene)-4-nitro-phenylmethanediamine (**3c**).* Yellow solid; mp 116–118 °C IR (KBr)/$\nu$ (cm$^{-1}$) 3400–3600 (br, OH), 1622 (s, C=N), 1480, 1570 (Ar), 1350, 1530 (N=O); $^1H$ NMR/DMSO/$\delta$ (ppm): 6.4 (s, 1H, NCHN), 6.5–7.6 (m, 12H), 8.9 (s, 2H, HC=N), 12.64 (s, 2OH); $^{13}C$ NMR/DMSO/$\delta$ (ppm): 89.9, 117.30, 119.6, 120, 124.9, 132.94, 134.2 148, 148.9, 160.9, 167; UV ($CHCl_3$)/$\lambda_{max}$ (nm) 323 (w), 262 (s); 262 (s); MS: $m/z = 376$ ($M^+ + 1$, 6), 375 ($M^+$, 10), 255 (65), 254 (80), 134 (85).

*3.3.1.4. N,N′-Bis(salicylidene)-2-hydroxy-phenylmethanediamine (**3d**).* Yellow solid; mp 164–166 °C; IR (KBr)/$\nu$ (cm$^{-1}$): 3250–3450 (br, OH), 1622 (s, C=N), 1450, 1550 (Ar); $^1H$ NMR/DMSO/$\delta$ (ppm): 6.1 (s, 1H, NCHN), 6.6–7.5 (m, 12H), 8.5 (s, 2H, HC=N); 9.7 (s, 1H, OH); 12.96 (s, 2OH); $^{13}C$ NMR/DMSO/$\delta$ (ppm): 90, 117, 120, 119.6, 127.5, 130.2, 130.3, 138, 165, 167; UV ($CHCl_3$)/$\lambda_{max}$ (nm) 322 (w), 261 (s); MS: $m/z = 348$ ($M^+ + 1$, 2), 347 ($M^+$, 8), 225 (55), 224 (65), 107 (70), 108 (100), 77 (20); Anal. Calcd. for C, H, N: 72.62 (C), 5.46 (H), 8.07 (N); found: 72.63 (C), 5.48 (H), 8.07 (N).

### *3.3.2. General procedure for the preparation of N,N′-2-arylmethanebis-(salicylaldiminato)uranil(II)*

To a solution of *N,N′*-bis(salicylidene)-phenylmethanediamine in MeOH (0.27 g, 0.7 mmol) was added $UO_2(O_2CCH_3)_2$ (0.32, 0.7 mmol) drop wise under mild conditions at room temperature. The reaction mixture was stirred to 1 h. The progress of the reaction was monitored by TLC. After the completion of the reaction, solid substance was obtained. The solid product was filtered off and washed with MeOH. The crude product was purified by recrystallization in ethanol and the pure Schiff base complex, *N,N′*-arylmethanebis-(salicylaldiminato)uranil(II) was obtained in 90–98% yield.

*3.3.2.1. N,N′-Phenylmethanebis-(salicylaldiminato)-cobalt(II) (**4a**).* Pale green solid; mp > 300 °C; IR (KBr)/$\nu$ (cm$^{-1}$) 1610 (s, C=N), 1450, 1550 (Ar); $^1$H NMR/DMSO/$\delta$ (ppm): 6.8 (s, 1H, NCHN), 6.8–7.7 (m, 13H), 8.9 (s, 2H, HC=N), 12.80 (s, 2OH); $^{13}$C NMR/DMSO/$\delta$ (ppm): 94, 118, 119, 119.5, 127.5, 130.1, 130.3, 138, 167, 172; MS: $m/z = 388$ ($M^+ + 1$, 0.5), 387 ($M^+$, 1.6), 330 (4), 331 (9), 210 (65), 209 (85), 91 (75), 89 (100); Anal. Calcd. for C, H, N: 65.12 (C), 4.13 (H), 7.23 (N); found:65.14 (C), 4.15 (H), 7.23 (N).

*3.3.2.2. N,N′-2-Methoxy-phenylmethanebis-(salicylaldiminato)-uranil(II) (**4b**).* Orange solid; mp > 300 °C; IR (KBr)/$\nu$ (cm$^{-1}$) 3375–3625 (br, OH), 1625 (s, C=N), 1450, 1510 (Ar); $^1$H NMR/DMSO/$\delta$ (ppm): 2.3 (3H, $OCH_3$), 6.2 (s, 1H, NCHN), 6.7–7.4 (m, 12H), 8.6 (s, 2H, HC=N), 12.90 (s, 2OH); $^{13}$C NMR/DMSO/$\delta$ (ppm): 60, 90, 117, 119, 119.2, 129.5, 130.2, 130.3, 138, 165, 170; UV ($CHCl_3$)/$\lambda_{max}$ (nm) 324 (w), 262 (s); MS: $m/z = 361$ ($M^+ + 1$, 8), 360 ($M^+$, 18), 241 (80), 240 (100), 119 (100), 120 (85); Anal. Calcd. for C, H, N: 42.04 (C), 2.87 (H), 4.46 (N); found: 42.06 (C), 2.9 (H), 4.46 (N).

*3.3.2.3. N,N′-4-Nitro-phenylmethanebis-(salicylaldiminato)-copper(II) (**4c**).* Green solid; mp > 300 °C IR (KBr)/$\nu$ (cm$^{-1}$) 1613 (s, C=N), 1470, 15650 (Ar), 1350, 1530 (N=O); $^1$H NMR/DMSO/$\delta$ (ppm): 6.8 (s, 1H, NCHN), 6.9–7.8 (m, 12H), 9.1 (s, 2H, HC=N); $^{13}$C NMR/DMSO/$\delta$ (ppm): 96.1, 117.30, 119.6, 120, 124.9, 132.94, 134.2 148, 148.9, 166.9, 174; MS: $m/z = 376$ ($M^+ + 1$, 12), 375 ($M^+$, 20), 255 (70), 254 (80), 134 (100), 91 (30); Anal. Calcd. for C, H, N: 57.66 (C), 3.43 (H), 9.61 (N); found: 57.68 (C), 3.45 (H), 9.62 (N).

*3.3.2.4. N,N′-2-Hydroxy-phenylmethane-bis-(salicylaldiminato)uranil(II) (**4d**).* Orange solid; mp 198–200 °C; IR (KBr)/$\nu$ (cm$^{-1}$): 1615 (s, C=N), 1445, 1550 (Ar); $^1$H NMR/DMSO/$\delta$ (ppm): 6.7 (s, 1H, NCHN), 6.8–7.6 (m, 12H), 9 (s, 2H, HC=N); 10.3 (s, 1H, OH); $^{13}$C NMR/DMSO/$\delta$ (ppm): 95, 117, 120, 119.6, 127.5, 130.2, 130.3, 138, 167, 170; MS: $m/z = 348$ ($M^+ + 1$, 2), 347 ($M^+$, 7), 225 (50), 224 (65), 107 (90), 108 (100); UV ($CHCl_3$)/$\lambda_{max}$ (nm) 324 (w), 263 (s); Anal. Calcd. for C, H, N: 41.11 (C), 2.45 (H), 4.57 (N); found: 41.12 (C), 2.5 (H), 4.58 (N).

## Acknowledgement

We are grateful to The University of Kashan Research Council for the partial support of this work.

## References

[1] (a) Nelson SM. Appl Chem 1980;52:2461;
(b) Bush DH, Vance AL, Kolchinski AG. In: Souvage J-P, Hosseini MW, editors. Comprehensive supramolecular chemistry, vol. 9. Oxford: Pergamon; 1996. p. 1–42;
(c) Vance AL, Alcock NW, Heppert JA, Busch DH. Inorg Chem 1998;37:6912.
[2] Ziessel R. Coord Chem Rev 2001;216–217:195.
[3] Alemi AA, Shaabani B. Acta Chim Slov 2000;47:363–9.
[4] Douce L, EL-Ghayoury A, Skoulios A, Ziessel R. Chem Commun; 1999;2033.
[5] You ZL, Zhu HL. Z Anorg Allg Chem 2004;630:2754.
[6] Goku A, Tumer M, Demirelli H, Wheatley RA. Inorg Chim Acta 2005;358:1785.
[7] Choudhury CR, Mondal SK, Mitrra S, Mahalli SDG, Malik KMA. J Chem Crystallogr 2002;31:57.
[8] Kolodziej AF. Prog Inorg Chem 1994;41:493.
[9] Parasher RK, Sharma RC, Kumar A, Mohan G. Inorg Chim Acta 1988;151:201.
[10] Chandra S, Saneetika X. Spectrochim Acta A 2004;60:147.
[11] (a) Samsel EG, Srinivasan K, Kochi J. J Am Chem Soc 1985;107:7606;
(b) Zhang W, Loebach JL, Wilson SR, Jacobsen ENJ. J Am Chem Soc 1990;112:2801;
(c) Irie R, Noda K, Ito Y, Matsumoto N, Katsuki T. Tetrahedron Lett 1990;31:7345;
(d) Sigman MS, Jacobsen ENJ. J Am Chem Soc 1998;120:4901.
[12] Atwood DA, Jegier JA, Rutherford DJ. J Am Chem Soc 1995;117:6779.
[13] Shamsipur M, Ghiasvand AR, Sharghi H, Naeimi H. Anal Chim Acta; 2000;271.
[14] Younkin TR, Connor EF, Henderson JI, Friedrich SK, Grubbs RH, Bansleben DA. Science 2000;287:460.
[15] Saito J, Mitani M, Matsui S, Mohri J, Kojoh S, Kashiwa N, et al. Angew Chem Int Ed Engl 2001;40:2918.
[16] Jones DJ, Gibson VC, Green S, Maddox MP. Chem Commun 2002;10:1038.
[17] O'Reilly RK, Gibson VC, White AJP, Williams DJ. J Am Chem Soc 2003;125:8450.
[18] Shamsipur M, Sadeghi S, Naeimi H, Sharghi H. Polish J Chem 2000;74:231.
[19] Alizadeh N, Ershad S, Naeimi H, Sharghi H, Shamsipur M. Ferseius' J Anal Chem 1999;365:511.
[20] Mazlum Ardakany M, Ensafi AA, Naeimi H, Dastanpour A, Shamlli A. Sensor Actuat B Chem 2003;441.
[21] Khorrami AR, Naeimi H, Fakhari AR. Talanta 2004;64:13.
[22] Shamsipur M, Yousefi M, Hosseini M, Ganjali MR, Sharghi H, Naeimi H. Anal Chem 2001;73:2869.
[23] Naeimi H, Safari J, Heidarnezhad A. Dyes Pigments, in press, doi:10.1016/j.dyepig.2005.12.009.
[24] Sharghi H, Naeimi H, Khaledi H. Iran J Chem Chem Eng 1999;18:72.
[25] Sharghi H, Naeimi H. Bull Chem Soc Jpn 1999;72:1525.