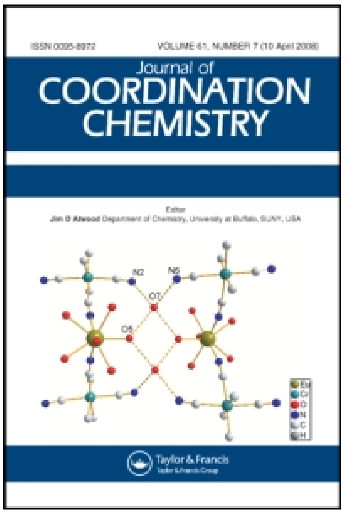

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# Template synthesis of some double Schiff-base metal(II) complexes through one pot four component reactions under mild and convenient conditions

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# Template synthesis of some double Schiff-base metal(II) complexes through one pot four component reactions under mild and convenient conditions

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Preparation of some Schiff-base complexes of Co(II), Cu(II), Ni(II) and $UO_2$(VI) from salicylaldehyde, ammonium hydroxide, aliphatic aldehydes and transition metal salts through one pot four component reaction are described. These complexes have been characterized by elemental analyses (C, H and N), infrared, $^1$H NMR, $^{13}$C NMR and mass spectroscopy.

*Keywords*: Schiff-base; Template; Four component; Complex; Aliphatic aldehydes

## 1. Introduction

Schiff bases contain an imine or azomethine; condensation of primary amines with carbonyl compounds yields Schiff bases [1, 2]. Interest in transition metal complexes of Schiff bases [3–5] is due to opportunities for inducing substrate chirality, tuning metal centered electronic factors and enhancing solubility and stability of homogenous or heterogeneous catalyst [6–11]. Schiff bases that have solvent dependent UV–Vis spectra (solvatochromicity) can be suitable NLO (non linear optical) active materials [12]. The presence of an electron pair on the nitrogen of the imino group enables coordination of numerous metal cations [13].

Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest [14] because of unusual configuration, structural lability and sensitivity to molecular environments [15]. Schiff-base complexes have been amongst the most widely studied coordination compounds and are becoming increasingly important as biochemical, analytical, and antimicrobial reagents [16]. Schiff-base complexes may provide synthetic models for metal-containing sites in metallo-proteins and enzymes [17]. These compounds also find catalytic applications ranging from asymmetric epoxidation [18], Lewis acid assisted organic transformations [19], solid phase extraction of metal ions [20], polymerization [21–24] and for preparation of ion selective electrodes [25–29].

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Template effects may arise from stereochemistry imposed by metal ion coordination of some of the reactants, promoting a series of controlled steps and characteristically provides routes to products not formed in the absence of the metal ion [30–31]. In view of this, recently, multicomponent reaction has much attention and many of them have been reported.

Ongoing work in our laboratory on the preparation of double Schiff-base complexes [32–36] found that multicomponent reaction of salicylaldehyde, aliphatic aldehyde, ammonium hydroxide and transition metal salts can yield efficient and convenient Schiff-base complexes.

In this study, we report a convenient one-pot synthesis of several Schiff-base complexes via template procedure under mild reaction conditions.

## 2. Experimental

### 2.1. *Materials*

All the materials were of commercial reagent grade. The salicylaldehyde, aliphatic aldehydes, ammonium hydroxide and transition metal salts were purchased from Merck Company and purified by standard procedures. The purity was determined by thin layer chromatography (TLC) and gas chromatography (GC).

### 2.2. *Apparatus*

IR spectra were recorded as KBr pellets on Perkin–Elmer 781 and Impact 400 Nicolet FTIR spectrophotometers. $^1$H and $^{13}$C NMR spectra were recorded in d$_6$-DMSO on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. Mass spectra were recorded on a Finnigan MAT 44S by electron ionization (EI) mode with an ionization voltage of 70 eV. The elemental analyses (C, H and N) were obtained from a Carlo ERBA Model EA 1108 analyzer.

Melting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reactions monitoring by the solvent system were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

### 2.3. *General procedure for preparation of Schiff-base metal(II) complexes*

To a solution of 3.0 mmols salicylaldehyde, 1.5 mmols aliphatic aldehyde and 3.0 mmols $NH_4OH$ in methanol (5 mL) was added 1.5 mmols $M(OAc)_2$ dropwise at room temperature by stirring in one portion; stirring is continued for 0.5 h. Progress of the reaction was monitored by TLC. After completion of the reaction, an orange solid was obtained. The solid product was filtered off, washed with cold methanol and purified by recrystallization in ethanol. Pure Schiff-base complexes, *N*,*N′*-1,1-alkanebis(salicylaldiminato)metal(II), were obtained in 90–98% yields and identified by physical and spectroscopic data.

**2.3.1. *N*,*N′*-1,1-[propanebis-(salicylaldiminato)]cobalt(II) (4a).** M.W. = 339 g ($C_{17}H_{16}N_2O_2Co$); pale red solid; m.p. = 310–313°C; IR (KBr)/$\upsilon$ (cm$^{-1}$) 3080, 2900, 1614 (s, C=N), 1437, 1530 (Ar), 1270 (C–O); $^1$H NMR/DMSO/$\delta$ p.p.m.: 0.9 (t, 3 H, $CH_3$), 2.1 (q, 2 H, $CH_2$), 4.97 (t, H, NCHN), 6.91–7.39 (m, 8 H, Ar), 8.8 (s, 2 H, HC=N); $^{13}$C NMR/$CDCl_3$/$\delta$ p.p.m.: 17, 25.2, 84, 117.3, 118.7, 119.5, 132.5, 134.1, 162, 165; MS: $m/z = 340$ ($M^+ + 1$, 2), 339 ($M^+$, 8), 283(5), 282(8), 162(30), 161(100), 58(100). Anal. Calcd for C, H, N: 60.18 (C), 4.72 (H), 8.26 (N). Found: 61.03 (C), 4.90 (H), 8.23 (N); UV ($CHCl_3$)/$\lambda_{max}$(nm) 234(s), 285(w).

**2.3.2. *N,N′*-1,1-[butanebis-(salicylaldiminato)]copper(II) (4b).** M.W. = 358 g ($C_{18}H_{18}N_2O_2Cu$); green solid; m.p. = 312–314°C; IR (KBr)/$\upsilon$ (cm$^{-1}$) 3080, 2910, 1614 (s, C=N), 1460, 1540 (Ar), 1278 (C–O); $^1$H NMR/DMSO/$\delta$ p.p.m.: 0.9 (t, 3 H, $CH_3$), 1.35 (q, 2 H, $CH_2$), 1.85 (q, 2 H, $CH_2$), 5.0 (t, H, NCHN), 6.91–7.6 (m, 8 H, Ar), 8.7 (s, 2 H, HC=N); $^{13}$C NMR/CDCl3/$\delta$ p.p.m.: 17, 17.3, 25.4, 85, 117.3, 118.7, 119.5, 132.5, 135.1, 162, 165; MS: $m/z = 359$ ($M^+$+1, 8), 358 ($M^+$, 10), 297(8), 296(11), 176(20), 175(100), 58(55). Anal. Calcd for C, H, N: 60.33 (C), 5.02 (H), 7.82 (N). Found: 61.09 (C), 5.07 (H), 7.82 (N); UV ($CHCl_3$)/$\lambda_{max}$(nm) 235(s), 287(w).

**2.3.3. *N,N′*-1,1-[hexanebis-(salicylaldiminato)]copper(II) (4c).** M.W. = 386 g ($C_{20}H_{22}N_2O_2Cu$); pale green solid; m.p. = 309–311°C; IR (KBr)/$\upsilon$ (cm$^{-1}$) 3090, 2900, 1615 (s, C=N), 1572, 1450 (Ar), 1284 (C–O); $^1$H NMR/DMSO/$\delta$ p.p.m.: 0.9 (t, 3 H, $CH_3$), 1.3 (m, 6 H, 3 $CH_2$), 1.85 (q, 2 H, $CH_2$), 5.0 (t, H, NCHN), 6.91–7.55 (m, 8 H, Ar), 8.69 (s, 2 H, HC=N); $^{13}$C NMR/$CDCl_3$/$\delta$ p.p.m.: 17, 17.3, 18.3, 18.4, 26.4, 86, 117.3, 118.7, 119.5, 132.5, 135.1, 162, 165; MS: $m/z = 387$ ($M^+ + 1$, 2), 386 ($M^+$, 6), 323(8), 322(12), 201(25), 200(100), 69(65), 58(55). Anal. Calcd for C, H, N: 62.17 (C), 5.69 (H), 7.26 (N). Found: 63.02 (C), 5.76 (H), 7.30 (N); UV ($CHCl_3$)/$\lambda_{max}$(nm) 236(s), 287(w).

**2.3.4. *N,N′*-1,1-[3-methylbutanebis-(salicylaldiminato)]cobalt(II) (4d).** M.W. = 367 g ($C_{19}H_{20}N_2O_2Co$); brown solid; m.p. = 310–312°C; IR (KBr)/$\upsilon$ (cm$^{-1}$) 3080, 2930, 2840, 1610 (s, C=N), 1500; 1586(Ar), 1275 (C–O); $^1$H NMR/DMSO/$\delta$ p.p.m.: 0.9 (d, 6 H, 2 $CH_3$), 1.5 (m, H, CH), 2 (t, 2 H, $CH_2$), 4.7 (t, H, NCHN), 6.91–7.6 (m, 8 H, Ar), 8.8 (s, 2 H, HC=N); $^{13}$C NMR/$CDCl_3$/$\delta$ p.p.m.: 17.3, 18.3, 18.4, 26.4, 86, 117.3, 118.7, 119.5, 132.5, 135.1, 162, 165; MS: $m/z = 368$ ($M^+ + 1$, 5), 367 ($M^+$, 10), 309(10), 308(15), 188(25), 185(100), 58(48). Anal. Calcd for C, H, N: 62.10 (C), 5.45 (H), 7.63 (N). Found: 63.01 (C), 5.50 (H), 7.64 (N); UV ($CHCl_3$)/$\lambda_{max}$(nm) 238(s), 287(w).

**2.3.5. *N,N′*-1,1-[isobutanebis-(salicylaldiminato)]uranyl(II) (4e).** M.W. = 564 g ($C_{18}H_{18}N_2O_4U$); orange solid; m.p. = 296–298°C; IR (KBr)/$\upsilon$ (cm$^{-1}$) 3100, 2900, 2870, 1610 (s, C=N), 1490; 1580(Ar), 1277 (CO); $^1$H NMR/DMSO/$\delta$ p.p.m.: 0.94 (d, 6 H, 2 $CH_3$), 2.1 (m, H, CH), 4.7 (d, H, NCHN), 6.92–7.53 (m, 8 H, Ar), 8.65 (s, 2 H, HC=N); $^{13}$C NMR/DMSO/$\delta$ p.p.m.: 17.3, 18.3, 18.4, 26.4, 86, 117.3, 118.7, 119.5, 132.5, 135.1, 162, 165; MS: $m/z = 565$ ($M^+ + 1$, 2), 564 ($M^+$, 6), 295(4), 294(12), 176(65); 175(100), 57(70). Anal. Calcd for C, H, N: 38.29 (C), 3.19 (H), 4.96 (N). Found: 39.03 (C), 3.21 (H), 4.97 (N); UV ($CHCl_3$)/$\lambda_{max}$(nm) 238(s), 287(w).

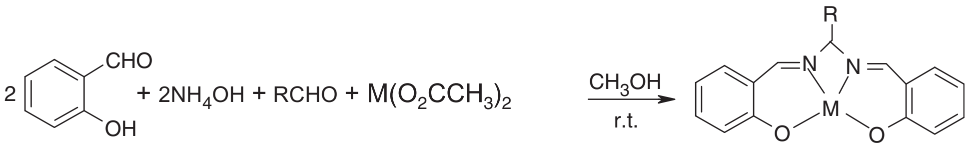
**2.3.6. *N,N′*-1,1-(3-phenylpropane)*bis*-(salicylaldiminato) nickel(II) (4f).** M.W. = 415 g ($C_{22}H_{19}N_2O_2Ni$); green; m.p. = 290–292°C; IR (KBr)/$\upsilon$ (cm$^{-1}$) 3100, 2930, 2840, 1620 (s, C=N), 1500; 1580(Ar), 1290 (CO); $^1$H NMR/DMSO/$\delta$ p.p.m.: 1.94 (t, 3 H, $CH_2$), 2.2 (q, 2 H, $CH_2$), 4.9 (t, H, NCHN), 6.7–7.9 (m, 13 H, Ar), 9 (s, 2 H, HC=N); $^{13}$C NMR/DMSO/$\delta$ p.p.m.: 17.3, 18.3, 18.4, 26.4, 86, 117.3, 118.7, 119.5, 132.5, 135.1, 162, 165; MS: $m/z = 416$ ($M^+ + 1$, 3), 415 ($M^+$, 6), 357(3), 356(12), 206(65); 118(62), 91(80). Anal. Calcd for C, H, N: 66.55 (C), 4.82 (H), 6.75 (N). Found: 67.02 (C), 4.89 (H), 6.77 (N); UV ($CHCl_3$)/$\lambda_{max}$(nm) 237(s), 286(w).

## 3. Results and discussion

Condensation between salicylaldehyde, aliphatic aldehyde, ammonium hydroxide and various transition metal salts in a single step leads to formation of a complex product. The complexes were characterized by spectroscopic and physical data. The reaction was carried out by mixing salicylaldehyde, aliphatic aldehyde, ammonium hydroxide and template transition metal ion at room temperature (scheme 1).

When 2 mol salicylaldehyde, 2 mol ammonium hydroxide, 1 mol aliphatic aldehyde and 1 mol transition metal salt were reacted, the corresponding products **4** were obtained (table 1). Schiff-base metal(II) complexes were afforded in high yields and short reaction times from the one pot reaction with transition metal ions such as $UO_2^{2+}$, $Co^{2+}$, $Cu^{2+}$ and $Ni^{+2}$. All the synthesized complexes are stable in air, soluble in DMSO, DMF, MeOH and EtOH, but poorly soluble in diethyl ether.

IR and UV–Vis data of the complexes are summarized in table 2. The infrared spectrum of the Schiff-base has a band at 1625 cm$^{-1}$ assignable to $\nu$(C=N) of azomethine [32], which shifts lower by about 10–15 cm$^{-1}$ on chelating with metal ion. In the Co(II) complex, the shift is more than the Cu(II) complex, perhaps because $Co^{2+}$ is harder than $Cu^{2+}$, leading to strong coordination with oxygen and nitrogens.



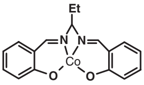
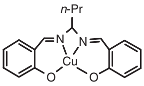
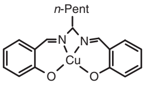
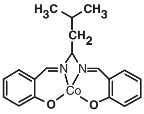
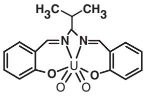
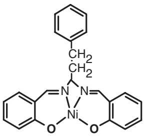
**1** **2** **3** **4a–f**

| | R | $M^{+2}$ |
|---|---|---|
| **4a** | $C_2H_5$ | Co |
| **4b** | $C_3H_7$ | Cu |
| **4c** | $C_5H_8$ | Cu |
| **4d** | $C_4H_9$ | Co |
| **4e** | $C_3H_7$ | $UO_2$ |
| **4f** | $PhC_2H_4$ | Ni |

Scheme 1. Synthesis of Schiff-base complexes.

The electronic spectra of all complexes showed intense absorptions in UV-region, which are assigned to charge transfer from the $\pi$ orbitals of the donor atoms to the d orbitals of the metal $d \rightarrow \pi^*$ [33] and intraligand $n \rightarrow \pi^*$ transitions [34]. In the complexes, the $n \rightarrow \pi^*$ transitions due to the azomethine group are shifted to lower

Table 1. The results of regarding to the reactions for preparation of Schiff-base complexes.

| Entry | Substrate | $M^{2+}$ | Product | Time (h) | M.P. (°C) | Yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 | $CH_3CH_2CHO$ | Co |  | 0.5 | 310–313 | 95 |
| 2 | $CH_3(CH_2)_2CHO$ | Cu |  | 1 | 312–314 | 95 |
| 3 | $CH_3(CH_2)_4CHO$ | Cu |  | 2 | 309–311 | 90 |
| 4 | $(CH_3)_2CHCH_2CHO$ | Co |  | 2 | 310–312 | 90 |
| 5 | $(CH_3)_2CHCHO$ | $UO_2$ |  | 0.5 | 296–298 | 98 |
| 6 | $Ph(CH_2)_2CHO$ | Ni |  | 1 | 290–292 | 96 |

[a] Isolated product yields based on salicylaldehyde.

Table 2. The IR and UV–Vis data of complexes.

| Entry | Product | IR ($cm^{-1}$) (C=N) | IR ($cm^{-1}$) (C–O) | IR ($cm^{-1}$) (C–C Ar) | UV ($\lambda_{max}$) |
|---|---|---|---|---|---|
| 1 | **4a** | 1604 | 1270 | 1437, 1530 | 234(s), 285(w) |
| 2 | **4b** | 1614 | 1278 | 1460, 1540 | 235(s), 287(w) |
| 3 | **4c** | 1615 | 1284 | 1572, 1450 | 236(s), 287(w) |
| 4 | **4d** | 1610 | 1275 | 1500, 1586 | 238(s), 287(w) |
| 5 | **4e** | 1610 | 1277 | 1490, 1580 | 238(s), 287(w) |
| 6 | **4f** | 1620 | 1290 | 1500, 1580 | 237(s), 286(w) |

energy, indicating the imine nitrogen coordinates to the metal [35]. The bands at 280–320 nm are assigned as $\pi \rightarrow \pi^*$ transitions involving molecular orbitals located on the phenol.

In $^1$H NMR spectra of Schiff bases [32, 36] in the free ligands, the broad signals around $\delta = 12.5$–$13.1$ ppm are assigned to protons of the hydroxyl groups. Two protons of CH=N have the same chemical shifts at $\delta = 8.5$–$8.9$ ppm. The signal at $\delta = 6.0$–$6.65$ ppm is assigned to protons of the NCHN and signals around $\delta = 6.6$–$7.90$ ppm are assigned to protons of aromatic rings (CH=CH). In the $^1$H NMR spectra of the Schiff-base complexes, all of these signals shift about 0.6 ppm to lower field and the broad signal around $\delta = 12.5$–$13.1$ ppm disappears.

In mass spectra, the molecular ion peak is assigned to formation of complexes. The patterns confirm their proposed structures. These data support the monomeric nature of complexes so that a dimeric structure is unlikely. The elemental analyses confirms their formation.

We report a convenient, efficient method for synthesis of Schiff-base complexes at room temperature using the template effect. The products have been afforded in excellent yields and short reaction times.

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