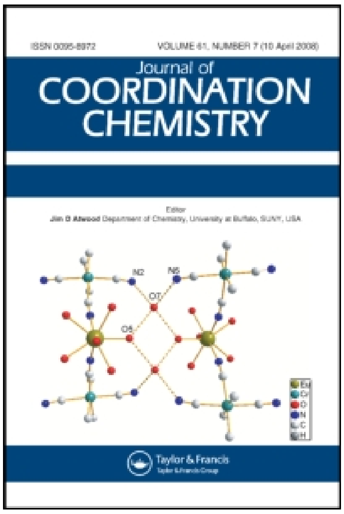

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Convenient, mild and rapid synthesis and characterization of some Schiff-base ligands and their complexes with uranyl(II) ion

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Convenient, mild and rapid synthesis and characterization of some Schiff-base ligands and their complexes with uranyl(II) ion

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Some Schiff-base complexes of UO_2(II) ion derived from 2-hydroxyacetophenone and aliphatic diamines under reflux conditions have been synthesized. The resulting ligands and their complexes have been characterized by elemental analyses (C, H, N), infrared, ^{1}H NMR, ^{13}C NMR and mass spectra. In these efficient reactions, Schiff-base complexes with important applications in analytical and organic chemistry are prepared.

Keywords: Schiff base; 2-Hydroxyacetophenone; Complex; Aliphatic amines

1. Introduction

Schiff-base ligands have been extensively studied in coordination chemistry due to their facile syntheses, easily tunable steric, electronic properties, good solubility in common solvents and numerous applications in organic synthesis and pharmacology [1]. Some Schiff bases have solvent dependent UV–Vis spectra (solvatochromicity) suitable for NLO (non-linear optical active) materials [2]. Schiff bases have applications in optical sensors [3], liquid crystals [4], chelating agents for nuclear medicine [5–10] and asymmetric catalysis [11, 12].

Organometallic complexes containing Schiff bases [13] have been used as catalysts for asymmetric cyclopropanation [14–17] and enantioselective aziridination [18]. Recently, bisbidentate Schiff-base metal complexes have been used as polymerization catalysts [19], in molecular hyperpolarizability studies [20] and for preparation of ion selective electrodes [21–25]. Various works have been published on uranyl Schiff-base compounds [26, 27].

We report the preparation of several Schiff-base complexes of uranyl(II) ion under mild conditions.

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2. Experimental

2.1. *Materials*

All the materials were of commercial reagent grade. The 2-hydroxyacetophenone and aliphatic diamine compounds were purified by standard procedures and purity determined by thin layer chromatography (TLC) and gas chromatography (GC).

2.2. *Apparatus*

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FTIR spectrophotometer. ^{1}H NMR 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, 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 reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

2.3. *General procedure for synthesis of 2,2′-[1,2–ethanediyl-*bis *(iminoethylidene)]-*bis*-phenol*

To a mixture of 2-hydroxyacetophenone (0.68 g, 5 mmol) in MeOH was added ethylene diamine (0.9 g, 2.5 mmol) and stirring for 15 min. The progress of the reaction was monitored by TLC. After reaction completion, yellow solid product was filtered off and washed with cold MeOH. The crude product was purified by recrystallization from ethanol and the pure Schiff base, 2,2′-[1,2–ethanediyl-*bis*(iminoethylidene)]-*bis*-phenol was obtained in 98% yield, m.p. = 190–192°C. The Schiff-base products were identified by physical and spectroscopic data.

2.3.1. 2,2′-[1,2-ethanediyl-*bis*(iminoethylidene)]*bis*-phenol (3a). Yellow solid; m.p. 190–192°C; IR (KBr)/ν(cm^{-1}): 3250–3600 (s, br, OH), 3050 (m, C–H, Ar), 1620 (s, C=N), 1450, 1500 (Ar); ^{1}H NMR/DMSO/δ ppm: 12.35 (s, 2H), 6.6–7.5 (m, 8H), 3.82 (s, 4H), 2.24 (s, 6H); ^{13}C NMR/DMSO/δ ppm: 172.50, 163.41, 132.53, 128.88, 120.40, 118.30, 117.39, 51.20, 18.56; MS: $m/z = 297$ ($M^{+} + 1$, 14), 296 (M^{+}, 30), 147 (75), 135 (100), 107 (45), 91 (44), Anal. Calcd for C, H, N: 72.97 (C), 6.75 (H), 9.45 (N); Found: 72.82 (C), 6.70 (H), 9.38 (N).

2.3.2. 2,2′-[1,3-propanediyl-*bis*(iminoethylidene)]*bis*-phenol (3b). Yellow solid; m.p. 181–119°C; IR (KBr)/ν(cm^{-1}): 3250–3600 (s, br, OH), 3070 (m, C–H, Ar), 1615 (s, C = N), 1425, 1500 (Ar); ^{1}H NMR/DMSO/δ ppm: 12.31 (s, 2H), 6.7–7.61 (m, 8H), 3.66 (t, 4H), 2.46 (s, 6H), 2.05 (q, 2H); ^{13}C NMR/DMSO/δ ppm: 172.50, 164.49, 132.18, 128.11, 119.43, 118.03, 116.81, 48.92, 28.95, 15.94; MS: $m/z = 311$ ($M^{+} + 1$, 14), 310 (M^+, 28), 162 (57), 148 (60), 136 (100), 107 (48), 91 (45), Anal. Calcd for C, H, N: 73.54 (C), 7.09 (H), 9.03 (N); Found: 73.50 (C), 7.00 (H), 8.98 (N).

2.3.3. 2,2′-[1,4-butanediyl-*bis*(iminoethylidene)]*bis*-phenol (3c). Yellow solid; m.p. 185–186°C; IR (KBr)/ν(cm^{-1}): 3250–3600 (s, br, OH), 3050 (m, C–H, Ar), 1615 (s, C=N), 1425, 1500 (Ar); ^{1}H NMR/DMSO/δ ppm: 12.32 (s, 2H), 6.7–7.71 (m, 8H), 3.60 (t, 4H), 2. 60 (s, 6H), 1.95 (t, 4H); ^{13}C NMR/DMSO/δ ppm: 172.50, 164.49, 132.18, 128.11, 119.43, 118.73, 116.81, 48.68, 28.04, 15.94; MS: $m/z = 325$ ($M^+ + 1$, 15), 324 (M^+, 30), 190 (34), 176 (40), 148 (60), 136 (100), 107 (38), 91 (45), Anal. Calcd for C, H, N: 68.18 (C), 7.40 (H), 8.64 (N); Found: 68.07 (C), 7.52 (H), 8.53 (N).

2.3.4. 2,2′-[1,6-hexanediyl-*bis*(iminoethylidene)]*bis*-phenol (3d). Yellow solid; m.p. 143–145°C; IR (KBr)/ν(cm^{-1}): 3250-3600 (s, br, OH), 3065 (m, C–H, Ar), 1625 (s, C=N), 1435, 1500 (Ar); ^{1}H NMR/DMSO/δ ppm: 12.3 (s, 2H), 6.2–7.61 (m, 8H), 3.60 (t, 4H), 2. 40 (s, 6H), 1.6 (t, 8H) MS: $m/z = 353$ ($M^+ + 1$, 8), 352 (M^+, 20), 190 (35), 176 (40), 162 (50), 148 (65), 136 (100), 107 (37), 91 (35), Anal. Calcd for C, H, N: 75 (C), 7.95 (H), 7.95 (N); Found: 74.85 (C), 7.90 (H), 7.89 (N).

2.3.5. 2,2′-[1,9-nonanediyl-*bis*(iminoethylidene)]*bis*-phenol (3e). Yellow solid; m.p. 80–82°C; IR (KBr)/ν(cm^{-1}): 3250–3600 (s, br, OH), 3000 (m, C–H, Ar), 1625 (s, C=N), 1405, 1500 (Ar), 1260 (C–O); ^{1}H NMR/DMSO/δ ppm: 12.33 (s, 2H), 6.6–7.5 (m, 8H), 3.50 (t, 4H), 2.35 (s, 6H), 1.65 (m, 4H), 1.41 (m, 4H), 1.33 (6H, s); ^{13}C NMR/DMSO/δ ppm: 172.79, 164.97, 132.63, 128.94, 119.43, 118.82, 116.67, 48.60, 30.73, 29.01, 28.89, 26.82, 14.82; MS: $m/z = 395$ ($M^+ + 1$, 6), 394 (M^+, 36), 176 (47), 162 (74), 148 (100), 136 (88), 107 (84), 91 (68), 77 (28), Anal. Calcd for C, H, N: 76.14 (C), 8.62 (H), 7.10 (N); Found: 76.02 (C), 8.51 (H), 7.00 (N).

2.4. *General procedure for synthesis of 2,2′-[1,2–ethanediyl-*bis *(imino-κ^2*N,N′*-ethylidene)]-*bis*(phenolato-κ^{2}O,O′) uranyl(II)*

To a solution of 2,2′-[1,2-ethanediyl-bis(iminoethylidene)]-*bis*-phenol (1 mmol) in MeOH (10 mL) was added $UO_2(O_2CCH_3)_2$ (1 mmol) dropwise under reflux. The reaction mixture was stirred 2 h and the progress monitored by TLC. After completion, yellow solid product was filtered off and washed with MeOH. The crude product was purified by recrystallization in ethanol giving 2,2′-[1,2-ethanediyl-*bis*(imino-$\kappa^2 N,N'$-ethylidene)]-*bis*(phenolato-$\kappa^2 O,O'$) uranyl(II) in 95% yield.

2.4.1. 2,2′-[1,2-ethanediyl-*bis*(imino-κ^{2}N,N′-ethylidene)]-*bis*(phenolato-κ^2*O,O′*) uranyl (4a). Yellow solid; m.p. 240–242°C, lit. [27] m.p. 237–239°C IR (KBr)/ν(cm^{-1}): 3050 (m, C–H, Ar), 1613 (s, C=N), 1427, 1531 (Ar); ^{1}H NMR/DMSO/δ ppm: 6.8–7.7 (m, 8H), 3.93 (t, 4H), 2.35 (s, 6H); ^{13}C NMR/DMSO/δ ppm: 172.50, 163.41, 132.53, 128.88, 120.40, 118.30, 117.39, 51.20, 18.56; MS: $m/z = 564$ (M^+, 3), 295 (8), 294 (12), 147 (60), 135 (100), 107 (30), 91 (25), Anal. Calcd for C, H, N: 38. 43 (C), 2.83 (H), 4.98 (N); Found: 38.32 (C), 2.74 (H), 4.88 (N).

2.4.2. 2,2′-[1,3-propanediyl-*bis*(imino-κ^2N,N′-ethylidene)]-*bis*(phenolato-κ^2*O,O*′) uranyl (4b). Yellow solid; m.p. 218–220°C; IR (KBr)/ν(cm^{-1}): 3070 (m, C–H, Ar), 1608 (s, C=N), 1450, 1540 (Ar); ^{1}H NMR/DMSO/δ ppm: 6.85–7.82 (m, 8H), 3.76 (t, 4H), 2.57 (s, 6H), 2.15 (q, 2H); ^{13}C NMR/DMSO/δ ppm: 172.50, 164.49, 132.18, 128.11, 119.43, 118.03, 116.81, 48.92, 28.95, 15.94; MS: $m/z = 580$ (M^+, 2), 311 (7), 310 (11), 162 (20), 148 (56), 136 (100), 107 (35), 91 (15), Anal. Calcd for C, H, N: 39.44 (C), 3.46 (H), 4.84 (N); Found: 39.35 (C), 3.39 (H), 4.71 (N).

2.4.3. 2,2′-[1,4-butanediyl-*bis*(imino-κ^2N,N′-ethylidene)]-*bis*(phenolato-κ^2*O,O*′) uranyl (4c). Yellow solid; m.p. 220–222°C; IR (KBr)/ν(cm^{-1}): 3090 (m, C–H, Ar), 1608 (s, C=N), 1460, 1540 (Ar); ^{1}H NMR/DMSO/δ ppm: 6.8–7.81 (m, 8H), 3.70 (t, 4H), 2.70 (s, 6H), 2.05 (t, 4H); ^{13}C NMR/DMSO/δ ppm: 172.50, 164.49, 132.18, 128.11, 119.43, 118.73, 116.81, 48.68, 28.04, 15.94; MS: $m/z = 594$ (M^+, 3), 325 (10), 324 (15), 190 (25), 148 (55), 136 (100), 107 (30), Anal. Calcd for C, H. N: 40.54 (C), 3.71 (H), 4.72 (N); Found: 40.48 (C), 3.62 (H), 4.63 (N).

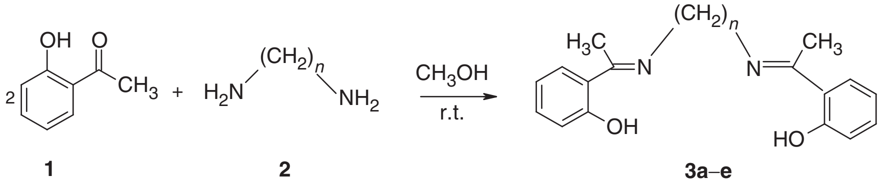
2.4.4. 2,2′-[1,6-hexanediyl-*bis*(imino-κ^2N,N′-ethylidene)]-*bis*(phenolato-κ^2*O,O*′) uranyl (4d). Yellow solid; m.p. 210–212°C; IR (KBr)/ν(cm^{-1}): 3050 (m, C–H, Ar), 1618 (s, C=N), 1454, 1541 (Ar); ^{1}H NMR/DMSO/δ ppm: 6.35–7.81 (m, 8H), 3.80 (t, 4H), 2. 50 (s, 6H), 1.72 (m, 8H); MS: $m/z = 622$ (M^+, 1), 353 (8), 352 (10), 190 (15), 176 (25), 148 (50), 136 (100), 107 (30), 91 (20), Anal. Calcd for C, H, N: 42.58 (C), 4.193 (H), 4.51 (N); Found: 42.49 (C), 4.190 (H), 4.46 (N).

2.4.5. 2,2′-[1,9-nonanediyl-*bis*(imino-κ^2N,N′-ethylidene)]-*bis*(phenolato-κ^2*O,O*′) uranyl (4e). Yellow solid; m.p. 82–84°C; IR (KBr)/ν(cm^{-1}): 3070 (m, C–H, Ar), 1618 (s, C=N), 1460, 1536 (Ar), 1250 (C–O); ^{1}H NMR/DMSO/δ ppm: 6.8-7.84 (m, 8H), 3.60 (t, 4H), 2.46 (s, 6H), 1.71 (t, 4H), 1.51 (m, 4H), 1.50 (6H, s); ^{13}C NMR/DMSO/δ ppm: 172.79, 164.97, 132.63, 128.94, 119.43, 118.82, 116.67, 48.60, 30.73, 29.01, 28.89, 26.82, 14.82; MS: $m/z = 664$ (M^+, 1), 395 (7), 394 (10), 176 (20), 148 (52), 136 (100), 107 (25), Anal. Calcd for C, H, N: 45.31 (C), 4.83 (H), 4.22 (N); Found: 45.27 (C), 4.78 (H), 4.12 (N).

3. Results and discussion

Some Schiff bases, 2,2′-[1,*n*-alkanediyl-*bis*(iminoethylidene)]-*bis*-phenol, have been prepared from 2-hydroxyacetophenone and various aliphatic diamines under mild reaction conditions in methanol (scheme 1). When 2 mols of 2-hydroxyacetophenone and 1 mol aliphatic diamine were reacted together, **3a**–**e** were obtained under mild conditions. The identity of these products were demonstrated by spectroscopic and physical data. The results of these reactions are shown in table 1.

We synthesized Schiff-base complexes by treatment of the Schiff bases with UO_2(II) under reflux, as represented in scheme 2. Ligand (1 mol) reacted with 1 mol UO_2^{2+}, giving products summarized in table 2. Schiff-base complexes of uranyl(II) were afforded in excellent yields and convenient reaction times. Most of the complexes are



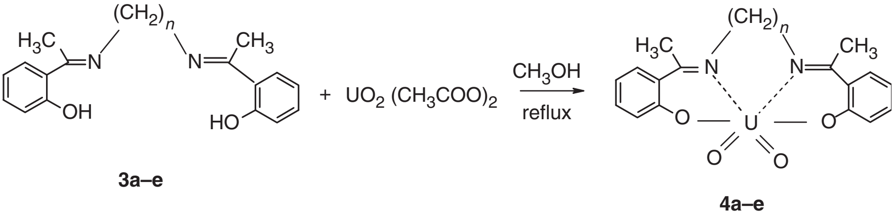
n=2, **3a**; n=3, **3b**; n=4, **3c**; n=6, **3d**, n=9, **3e**

Scheme 1. Preparation of Schiff bases from 2-hydroxyacetophenone.

Table 1. Results related to the synthesis of Schiff bases.

Entry	Substrate	Product	Time (min)	M.P. (°C)	Yield[a] (%)
1	$H_2N–(CH_2)_2–NH_2$	**3a**	5	190–192	95
2	$H_2N–(CH_2)_3–NH_2$	**3b**	5	118–119	97
3	$H_2N–(CH_2)_4–NH_2$	**3c**	10	185–186	95
4	$H_2N–(CH_2)_6–NH_2$	**3d**	10	143–145	95
5	$H_2N–(CH_2)_9–NH_2$	**3e**	15	80–82	90

[a]Isolated yields based on ketone.



n=2, **4a**; n=3, **4b**; n=4, **4c**; n=6, **4d**; n=9, **4e**

Scheme 2. Synthesis of Schiff-base complexes of uranyl(II).

Table 2. Results for preparation of Schiff-base complexes.

Entry	Substrate	Product	Time (h)	M.P. (°C)	Yield[a] (%)
1	**3a**	**4a**	2	240–242	95
2	**3b**	**4b**	2	218–220	98
3	**3c**	**4c**	2	220–222	95
4	**3d**	**4d**	3	210–212	90
5	**3e**	**4e**	3.5	82–84	95

[a]Isolated yields based on Schiff base.

colored, stable in air, soluble in DMSO, DMF, MeOH and EtOH, but poorly soluble in diethyl ether.

Structures of the resulting Schiff bases and their complexes have been assigned by physical and spectroscopic data. The infrared spectra of the Schiff bases exhibit a band at 1605–1625 cm^{-1} assignable to $\nu_{C=N}$ of azomethine. This band shifts lower by 7–15 cm^{-1} on the chelation of ligand with metal ion.

In the ^{1}H NMR spectra of the free ligands, the broad signal around $\delta = 12.30$–12.35 ppm is assigned to hydroxyl groups and signals around $\delta = 6.20$–7.71 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 to lower field and the broad signal around $\delta = 12.30$–12.35 ppm disappears, proving complex formation of ligand with uranyl ion.

In ^{13}C NMR spectra, the signal about $\delta = 172.5$ ppm is assigned to the carbon of imine (C=N), the aromatic carbons are between $\delta = 116$–164 ppm and aliphatic carbons are between $\delta = 15$–48 ppm.

In mass spectra of ligands, the molecular ion is present. In the complexes, weak molecular ions indicating monomeric structures appear. Mass spectra are the only data that support monomers for the complexes, and based on these data, a dimeric structure is unlikely. Finally, the elemental analyses confirmed the formation of ligands and their complexes.

In conclusion, we report a mild and convenient synthesis of Schiff-base complexes of UO_2(II). The Schiff bases for preparation of these complexes have been obtained through simple and efficient reaction of 2-hydroxyacetophenone with aliphatic diamines. The products are prepared in excellent yields and convenient reaction times.

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