

Dioxouranium(VI) nitrate complexes of some schiff bases derived from furfural & 2-acetylfuran with certain amino compounds

G Sobhanadevi & P Indrasenan*

Department of Chemistry, University of Kerala, Trivandrum
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Dioxouranium(VI) nitrate complexes with 10 schiff bases obtained by the condensation of furfural and 2-acetylfuran with isonicotinoylhydrazine, benzoylhydrazine, salicyloylhydrazine, anthranilic acid, and 4-aminoantipyrine have been synthesized and characterized on the basis of IR spectra, conductance, magnetic, elemental analyses and molecular weight data.

In continuation of our early work on schiff base complexes of dioxouranium(VI)¹⁻³, we report herein the synthesis and characterization of ten new dioxouranium(VI) nitrate complexes of schiff bases obtained by the condensation of furfural and 2-acetylfuran with isonicotinoylhydrazine, benzoylhydrazine, salicyloylhydrazine, anthranilic acid and 4-aminoantipyrine. The schiff bases derived from furfural have the structures (1-3, 7 and 9), while those from 2-acetylfuran have the structures (4-6, 8 and 10).

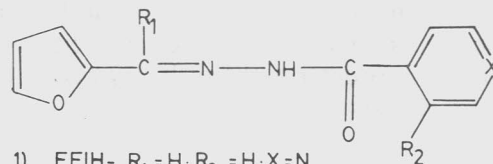
Experimental

Uranyl nitrate (BDH, AR; 99.9% pure) was used as such and the ten schiff bases (1-10) were prepared by mixing furfural (or 2-acetylfuran) with each of the five amino compounds mentioned earlier, in ethanol in the molar ratio 1:1 and refluxing on a water bath for 5 hr. The ligands, which crystallized out on concentration were filtered, washed successively with ethanol and diethylether and dried *in vacuo* over phosphorus(V) oxide. The purities of the ligands were checked by TLC, IR spectra and melting points.

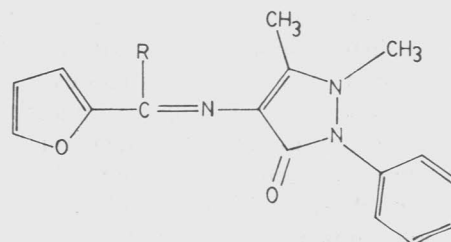
The complexes were prepared as follows: Solutions of uranyl nitrate (2 mmol) and the schiff base (4.1 mmol) in hot acetonitrile (for FFIH, FFSH, FFAA, AFIH, AFSH and AFAA) or in hot methanol (for FFBH, FFAAP, AFBH and AFAAP) were mixed and refluxed on a water-bath for 3-4 hr. On concentration the complexes of FFIH, FFSH, FFAA, FFAAP and AFIH crystallized out and were filtered and washed with minimum amounts of hot acetonitrile or methanol. Complexes of FFBH, AFAA, AFSH, and

AFBH were precipitated by adding chloroform to the viscous mass obtained on concentration of the solution. The solids obtained were filtered and washed with small quantity of hot chloroform. The AFAA and AFSH complexes were dissolved in minimum amounts of hot acetonitrile and crystallized out by adding diethylether and collected. The FFBH and AFBH complexes were dissolved in minimum amount of hot methanol, and crystallized out by adding chloroform and collected. In the case of AFAAP complex the viscous mass was washed repeatedly with benzene, dissolved in hot methanol and crystallized out by adding benzene and collected. All the complexes were dried *in vacuo* over phosphorus(V) oxide.

Molar conductances of 10⁻³M solutions of the complexes in acetonitrile, methanol and nitrobenzene were determined at room temperature (28 ± 2°C) on the ELICO conductivity bridge type CM82 with a dip-type cell having platinum electrodes (cell constant, 1.33). The IR spectra of the ligands and the complexes were recorded in KBr in the range of



- 1) FFIH- R₁ = H; R₂ = H; X = N
- 2) FFBH- R₁ = H; R₂ = H; X = C
- 3) FFSH- R₁ = H; R₂ = -OH; X = C
- 4) AFIH- R₁ = -CH₃; R₂ = H; X = N
- 5) AFBH- R₁ = -CH₃; R₂ = H; X = C
- 6) AFSH- R₁ = -CH₃; R₂ = -OH; X = C
- 7) FFAA- R₁ = H; R₂ = -COOH; X = C
- 8) AFAA- R₁ = CH₃; R₂ = -COOH; X = C



- 9) FFAAP- R = H
- 10) AFAAP- R = -CH₃

Table 1—Analytical, molecular weight and conductance data of uranyl nitrate complexes of some schiff bases

Compound	Found (calc.)%				Mol. wt. Found (Calc.)	Molar conductance		
	M	C	H	N		Acetonitrile	Methanol	Nitrobenzene
[UO ₂ (FFIH)(NO ₃) ₂]	39.00 (39.08)	21.11 (21.67)	1.56 (1.48)	11.01 (11.49)	600 (609)	26.39	70.37	7.66
[UO ₂ (FFBH)(NO ₃) ₂]	38.99 (39.15)	23.44 (23.68)	2.00 (1.64)	8.92 (9.21)	598 (608)	14.95	74.49	6.50
[UO ₂ (FFSH)(NO ₃) ₂]	37.91 (38.14)	23.00 (23.08)	1.67 (1.60)	8.09 (8.97)	592 (624)	19.11	76.70	8.75
[UO ₂ (FFAA) ₂]	33.95 (34.05)	33.99 (41.26)	2.61 (2.29)	3.97 (4.01)	—	10.92	39.00	2.28
[UO ₂ (FFAAP) ₂ (NO ₃) ₂]	24.80 (24.90)	39.89 (40.17)	3.77 (3.14)	11.03 (11.72)	1001 (952)	24.96	86.71	8.26
[UO ₂ (AFIH)(NO ₃) ₂]	37.58 (38.20)	22.78 (23.11)	2.42 (1.77)	10.59 (11.23)	—	10.53	55.90	5.59
[UO ₂ (AFBH)(NO ₃) ₂]	37.93 (38.26)	25.41 (25.08)	2.50 (1.93)	8.75 (9.00)	565 (622)	20.12	79.89	5.91
[UO ₂ (AFSH)(NO ₃) ₂]	36.75 (37.30)	23.16 (24.45)	2.91 (1.88)	9.44 (8.78)	—	8.74	21.06	4.94
[UO ₂ (AFAA) ₂]	32.44 (32.78)	42.59 (42.98)	3.01 (2.75)	3.51 (3.87)	790 (726)	3.77	68.77	5.30
[UO ₂ (AFAAP) ₂ (NO ₃) ₂]	23.66 (24.19)	41.10 (41.46)	3.81 (3.46)	10.99 (11.38)	1018 (984)	30.79	90.13	7.16

4000-400 cm⁻¹ on a double beam Perkin-Elmer 397 IR spectrophotometer. The molecular weights of the complexes were determined by the cryoscopic method in nitrobenzene⁴.

Results and discussion

The complexes listed in Table 1 are brownish-yellow or orange-yellow coloured, non-hygroscopic crystalline solids. Molar conductances of the complexes indicate them to be non-electrolytes implying that the nitrate ions are coordinated to the metal ion⁵. The analytical, molecular weight and conductance data suggest that the complexes can have the compositions: UO₂L₂(NO₃)₂ (where L = FFAAP and AFAAP), UO₂L₂ (where HL = FFAA and AFAA) and UO₂L(NO₃)₂ (where L = FFIH, FFBH, FFSH, AFIH, AFBH and AFSH).

The IR spectra of the schiff bases (**1-10**) exhibit the $\nu\text{C}=\text{N}$ mode in the region of 1580-1610 cm⁻¹. In the spectra of the complexes the $\nu\text{C}=\text{N}$ modes appear at lower wavenumber (1595-1560 cm⁻¹) indicating that the ligands are coordinated to the metal ion through the azomethine nitrogen. In the spectra of all the ligands, except those of FFAAP and AFAAP, the $\nu\text{C}=\text{O}$ mode appear in the region of 1660-1620 cm⁻¹, which is shifted to 1620-1600 cm⁻¹ in the spectra of their complexes suggesting that the side chain carbonyl group is also coordinated to the metal

ion. The IR spectra of FFAAP and AFAAP exhibit the $\nu\text{C}=\text{O}$ (ring) at 1640 cm⁻¹, which is shifted to 1610 cm⁻¹ in the corresponding complexes indicating that the ring carbonyl group of these ligands is involved in coordination.

In the IR spectra of FFSH and AFSH and their complexes the $\nu\text{O}-\text{H}$ appears as a broad band at 3450 cm⁻¹ indicating that the OH group does not participate in coordination. The $\nu\text{O}-\text{H}$ (carboxylate ion) of FFAA and AFAA appears as a strong band at 3000 cm⁻¹. This mode is absent in the spectra of their complexes suggesting that the carboxylic acid is coordinated to the metal ion after deprotonation. This is further supported by the disappearance of the band at 1650 (for FFAA) or at 1660 (for AFAA) cm⁻¹ in the spectra of the FFAA and AFAA complexes and the elimination of the two nitrate ions in these two complexes. The bands observed at 1610-1600 and 1410-1380 cm⁻¹ in the spectra of the complexes of FFAA and AFAA are assigned to $\nu_{\text{as}}\text{OCO}$ and $\nu_{\text{s}}\text{OCO}$, respectively of the carboxylate ion. Since the difference, $\nu_{\text{as}}-\nu_{\text{s}}$ is in the range of ~ 220 cm⁻¹, the carboxylate ion is coordinated to the metal ion in a monodentate fashion^{6,7}. The bands due to furan ring observed at 1500 and 880 cm⁻¹ in the spectra of all the ligands remain unaltered in the spectra of the complexes suggesting that the furan ring oxygen does not participate in coordination⁸.

In the IR spectra of all the complexes except those of FFAA and AFAA, four additional bands are observed at 1460-1500, 1240-1290, 1030 and 915-930 cm^{-1} . The first three bands are assigned to ν_4 , ν_1 and ν_2 modes, respectively of coordinated nitrate ion. Since the magnitude of separation, $\nu_4-\nu_1$ is $\sim 240 \text{ cm}^{-1}$, the nitrate ions present in these eight complexes are coordinated to the uranyl ion in a bidentate fashion⁹. The fourth additional band appearing at $915-930 \text{ cm}^{-1}$ is also present in the spectra of the complexes of FFAA and AFAA and this band is assigned to ν_3 mode of O = U = O group. The absence of the symmetric mode (ν_1) of O = U = O group in the spectra of all the complexes suggests that the linearity of UO_2^{2+} ion is maintained in the complexes also and hence the two oxygen atoms of the UO_2^{2+} ion are in the *trans* position in the complexes¹⁰.

On the basis of the above observations all the ligands, except FFAA and AFAA act as neutral bidentate ones, whereas FFAA and AFAA act as monobasic terdentate ones. A coordination number of 10 is assigned to the uranium ion in the FFAAP and AFAAP complexes, and a coordination number of 8 for

the complexes of FFIH, FFBH, FFSH, FFAA, AFIH, AFBH, AFSH and AFAA.

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Table 1 - Analytical data of the complexes

Complex	Element	Found (%)	Calc. (%)
[UO ₂ (H ₂ O) ₂ (FFAH)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (FFBH)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (FFSH)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (FFAA)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (AFIH)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (AFBH)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (AFSH)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78
[UO ₂ (H ₂ O) ₂ (AFAA)]	C	47.83	47.83
	H	3.63	3.63
	N	4.78	4.78