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Synthesis and Spectral Characteristics of Dioxouranium(VI) Complexes with Furohydroxamic Acid and N-Phenyl Furohydroxamic Acid

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Some dioxouranium(VI) complexes of furohydroxamic acid and N-phenyl furohydroxamic acid have been synthesized and characterized by elemental analysis, magnetic susceptibility measurements, IR and electronic spectral data. An octahedral geometry has been assigned to both the isolated complexes

Key Words: UO_2(VI), Comples, Furohydroxamic acid, N-phenyl furohydroxamic acid.

INTRODUCTION

Hydroxamic acids are naturally occurring compounds that follow the formula RCON-R'OH (R, R' = H, aryl or alkyl) and usually exhibit biological activity. Some of them are antibacterial, antifungal, anticancer, antibiotic agents and specific enzyme inhibitors[1-3]. As iron chelators, siderophores have applications for iron-related diseases. The metal complexing character of hydroxamic acids makes them useful for analytical applications as well[4]. In the present paper, we report the synthesis and characterization of furohydroxamic acid (FHA) and N-phenyl furohydroxamic acid (NPFHA).

EXPERIMENTAL

All the chemicals used were of AR grade.

Synthesis of Ligands

(I) Preparation of Furohydroxamic Acid (FHA)

An aqueous solution of 5.30 g (0.05 M) sodium carbonate in 25 mL of water was added to 25 mL ethereal solution of 3.47 g (0.05 M) of finely powdered hydroxylamine hydrochloride. This mixture was stirred well using a mechanical stirrer and the temperature of the mixture was maintained to about 0°C by external cooling using freezing mixture. Furoyl chloride 6.25 mL (0.05 M) in 25 mL diethyl ether was added to this mixture very slowly (in *ca.* 1 h) with constant stirring. After the complete addition of furoyl chloride solution, the stirring was

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continued for another 30 min. Almost 80% of the product was precipitated during the process of the reaction. Some of the product, which was dissolved in ether layer during the process of coupling reaction, was recovered from the ether layer by distillation under reduced pressure. The total product was triturated with sodium hydrogen carbonate and then repeatedly washed with cold water to remove the acidic impurities.

The crude furohydroxamic acid thus obtained was dissolved in ethyl acetate and the recrystallized furohydroxamic acid was obtained by keeping the filtered product at room temperature and dried over P_2O_5 in a vacuum desiccator. Yield: 9.60 g (crude); 6.20 g (recrystallized).

(II) Preparation of N-Phenyl Furohydroxamic Acid (NPFHA)

An aqueous solution of 5.3 g (0.05 M) of sodium carbonate in 25 mL of water was added to 25 mL ethereal solution of 5.45 g (0.05 M) of finely powdered phenyl hydroxylamine. This mixture was stirred well using a mechanical stirrer and the temperature of the mixture was maintained at about 0°C by external cooling using freezing mixture. Furoyl chloride 6.25 mL (0.05 M) in 25 mL diethyl ether was added to this mixture very slowly (in *ca.* 1 h) with constant stirring. After the complete addition of furoyl chloride solution, the stirring was continued for 30 min. Almost 80% of the product was precipitated during the process of reaction. Some of the product, which was dissolved in ether layer during the process of coupling reaction was recovered from the ether layer by distillation under reduced pressure. The total product was triturated with sodium hydrogen carbonate and then repeatedly washed with cold water to remove the acidic impurities.

The crude N-phenyl furohydroxamic acid thus obtained was dissolved in ethyl acetate and the recrystallised N-phenyl furohydroxamic acid was obtained by keeping the filtered product at room temperature and were dried over P_2O_5 in a vacuum desiccator. Yield: 8.65 g (crude); 4.30 g (recrystallized).

Preparation of Metal Complexes

10 mL alcoholic solution of 1.27 g (0.01 M) FHA or 2.03 g (0.01 M) NPFHA was added to 10 mL aqueous solution of 2.12 g (0.005 M) uranyl acetate in a round bottom flask. The solution was stirred for 10 min and refluxed on a water bath for about 3 h; 2 mL ammonia solution was slowly added to this solution and again refluxed for 1 h. After this the hot solution was filtered and the filtrate was kept at room temperature for crystallization. The crystals were obtained after 24 h, which were washed with water, alcohol and followed by ether. Finally the crystals were dried over P_2O_5 in a vacuum desiccator.

The uranium metal[5] was estimated by using 8-hydroxy quinoline. The elemental analysis of carbon, hydrogen and nitrogen, infrared spectra of the ligand and their metal complexes were recorded in KBr on Perkin-Elmer 577 spectrophotometer in the region *ca.*4000–200 cm^{-1}, mass spectra of the ligands were recorded in the region 50–350 MHz, NMR spectra of the ligands were recorded at RSIC, CDRI Lucknow. Magnetic susceptibility measurements of the synthesised complexes were carried out the room temperature on EG & G Model

155 VSM (vibrating sample magnetometer) at RSIC, IIT, Chennai. The electronic spectra of complexes in solution (H_2O/DMF) were recorded on Systronics-106 at room temperature at the Department of Chemistry, R.B.S. College, Agra.

RESULTS AND DISCUSSION

Characterisation of the Ligands

(a) FuroHydroxamic Acid (FHA): m.f. = $C_5H_5NO_3$, m.p. = 115°C. IR spectra: bands at *ca.* 3155 ν(N—OH), *ca.* 1595 ν(C=O), *ca.* 1361 ν(C—N), *ca.* 904 ν(N—O) and *ca.* 1283 cm^{-1} ν(C—O—C). Mass Spectra: m/e 127 (M^+), 110 (M^+), 95 (M^+), 68 (M^+). Elemental analysis: % Found (calculated): C = 45.66 (47.24), H = 3.19 (3.93), N = 10.48 (11.02). NMR Spectra: Chemical shifts were (observed as singlet), furan due to proton 6.30 and 7.40, NH—C—R 7.53, N—H aromatic proton 4.12.

(b) N-Phenyl Furohydroxamic Acid (NPFHA): m.f. = $C_{11}H_9NO_3$, m.p. = 65°C. IR Spectra: bands at *ca.* 3150 ν(N—OH), *ca.* 1598 ν(C=O), *ca.* 1351 ν(C—N), *ca.* 917 ν(N—O) and *ca.* 1282 cm^{-1} ν(C—O—C). Mass Spectra: m/e 203 (M^+), 186 (M^+), 126 (M^+), 95 (M^+) and 68 (M^+). Elemental analysis: % Found (calculated): C = 65.49 (65.02), H = 4.04 (4.43), N = 5.57 (6.89). NMR spectra: Chemical shifts were (observed as singlet), furan due to proton 6.37 and 7.41, NH—C—R 7.51, N—H aromatic proton due to phenyl ring 7.26–7.68.

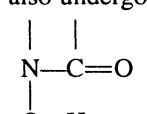
The analytical results, melting points, colour and magnetic moments of the complexes are presented in Table-1.

Both the uranyl complexes are found to be diamagnetic (μ_{eff} = 0.59 B.M.) depending upon the diamagnetism of the other ions and the surrounding ligand field. The ground state of uranyl(VI) compounds contains no unpaired electrons.

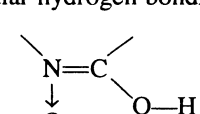
Important IR frequencies of both the complexes are given in Table-2.

A broad IR band (*ca.* 3155 cm^{-1}) in the complexes indicates the presence of hydroxamic OH group[6], which is further established by the presence of ν(N—OH) in both complexes[7]. Phenolic hydroxyl groups deprotonate[8] to bind the central metal atom and thus cannot result into O—H bond as in the free ligand.

Hydroxamic acids may exist in two geometrical isomeric forms *cis* and *trans* with respect of the partial double bond character of C—N bond. This class of compounds can also undergo intermolecular hydrogen bonding[9, 10].



cis (I)



trans (II)

The ν(C=O) frequencies of hydroxamic acid in general occur at 1610, 1680 cm^{-1} and do not correspond to the free carbonyl frequencies (1700 cm^{-1}) indicating the presence of hydrogen bonding. An intramolecular hydrogen bonded

TABLE-1
PHYSICAL PROPERTIES, ANALYTICAL DATA AND MAGNETIC MOMENT VALUES OF URANYL COMPLEXES

Complexes	Physical properties				Analytical data %, found (Calcd.)				μ_{eff} (B.M.)
	m.p. (°C)	Colour	m.w.	State	C	H	N	U	
$UO_2(C_5H_5NO_3)_2$ $(CH_3COO)_2$	225	brown	615.30	solid (powder)	27.32 (27.39)	2.64 (2.73)	3.84 (3.99)	33.80 (33.93)	0.62
$UO_2(C_{11}H_9NO_3)_2$ $(CH_3COO)_2$	265	brownish yellow	853.54	solid (crystalline)	39.29 (39.40)	3.10 (3.18)	3.19 (3.28)	27.78 (27.88)	0.59

TABLE-2
KEY INFRARED SPECTRAL BANDS (cm^{-1}) OF URANYL COMPLEXES

Complexes	Assignments					Uranyl Modes		
	ν(N—OH)	ν(C=O)	ν(C—N)	ν(N—O)	ν(CH_3COO—)	ν_{asym} (O=U=O)	ν_{sym} (O=U=O)	ν(U—O)
$UO_2(C_5H_5NO_3)_2(CH_3COO)_2$	3152b	1587b	1407m	1016s	1473s	955w	864s	474s
$UO_2(C_{11}H_9NO_3)_2(CH_3COO)_2$	3138b	1548m	1413m	1039s	1477s	958m	905s	462s

carbonyl group absorbs at a lower frequency than the corresponding intermolecular hydrogen bonded carbonyl group. In addition, when hydrogen bonding is intramolecular the O—H stretching band is usually broad, whereas a relatively sharp hydroxyl absorption band is generally obtained when hydrogen bonding is intermolecular[11]. The involvement of ketonic oxygen complex formation is shown by the lowering of carbonyl group frequency from 1595 cm^{-1} to 1587 cm^{-1} in the complex formation.

The C—N stretching frequency[12] (1361 cm^{-1}) in the free ligand is found to be displaced towards higher frequency on complexation. These observations show that coordination of hydroxamic acid occurs through oxygen of carbonyl group. The band due to N—O stretching vibration[13] (900–910 cm^{-1}) in free ligand gets shifted to higher frequency *ca.*1040 cm^{-1} on complexation. The bonding of carbonyl oxygen to uranium ion has been further confirmed by appearance of (U—O) stretching frequency at 474 and 462 cm^{-1}. The presence of uranium oxygen covalent bond in the complex was established by observation of bands at 950–900 cm^{-1} in the complex. This band is assigned to IR, active non-degenerate asymmetric stretching mode of uranyl ion, *i.e.*, ν_3. The non-degenerate symmetric stretching ν_1 band present at 870–815 cm^{-1} in the complex indicates the linearity of the UO_2^{2+} entity (O=U=O). A strong band at 904 and 917 cm^{-1} in ligand due to ν(N—O) frequency is overlapped or coupled with ν_1 mode of uranyl ion. On the basis of IR spectra we can say that the uranium(VI)[14, 15] is octahedrally coordinated to two ligand molecules and two oxygen atoms.

The force constants and U—O bond distance were calculated by using Wilson's[16] FG matrix and Badger[17] formula respectively and are presented in Table-3, which are in good agreement with the available data of dioxouranium(VI) complexes.

TABLE-3
ABSORPTION FREQUENCIES, FORCE CONSTANTS AND BOND LENGTH OF URANYL COMPLEXES

S.No.	Complexes	U—O force constant (m dyne/Å)	Force constant due to interaction between bonds (m dyne/Å)	U—O bond distance (Å)	ν_1 (cm^{-1})	ν_2 (cm^{-1})
1.	$UO_2(C_5H_5NO_3)_2(CH_3COO)_2$	7.1433	–0.1058	17377	872	955
2.	$UO_2(C_{11}H_9NO_3)_2(CH_3COO)_2$	7.0718	–0.0047	17325	905	958

The visible spectra of the complexes were recorded in the DMF against solvent blanks. The spectra show no band in the region 400–700 nm indicating no transitions due to *f*-electrons. This indicates f^0-configuration of the metal ion. The complexes were of diamagnetic nature which supports f^0-configuration. In present studies the octahedral geometry of both complexes have been assigned.

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