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Synthesis and Characterization of Dioxouranium(VI) Complexes of β-Substituted Hydrazones of Acetoacetanilide

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SYNTHESIS AND CHARACTERIZATION OF DIOXOURANIUM(VI) COMPLEXES OF β -SUBSTITUTED HYDRAZONES OF ACETOACETANILIDE

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ABSTRACT

Dioxouranium(VI) complexes with four ligands which were obtained by the condensation of acetoacetanilide with benzoyl-, salicyloyl- and isonicotinoylhydrazines and semicarbazide hydrochloride, have been synthesized and characterized on the basis of elemental analyses, molar conductance and magnetic measurements as well as electronic and IR spectral studies. They were found to have the general composition $[UO_2L_2X_2]$, where L = benzoyl- (AaBH), salicyloyl- (AaSH) and isonicotinoyl- (AaINH) hydrazones or semicarbazone (AaSCH) of acetoacetanilide and X = NO_3^- or CH₃COO⁻. The hydrazones and semicarbazone act as neutral bidentate ligands bonding through the anilide carbonyl oxygen and azomethine nitrogen atoms and the nitrate and the acetate anions coordinate in a monodentate fashion.

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INTRODUCTION

Multidentate hydrazones are of considerable research interest because of their ability for chelation with metal ions forming complexes with biological activity. Aroylhydrazones are characterized by the CONH-N=C group which imparts antiparasitic, fungicidal and bactericidal properties to them^{1,2}. Uranium complexes of hydrazones received much interest because of their high stability and usefulness in selective chemical separations. Our literature survey revealed that reports on complexes of hydrazones of diketones with oxocations, in general, and dioxouranium(VI), in particular, are scanty^{3,4}. We report herein the synthesis and characterization of uranyl nitrate and acetate complexes of benzoyl- (AaBH), salicyloyl- (AaSH) and isonicotinoyl- (AaINH) hydrazones and semicarbazone (AaSCH) of acetoacetanilide (Fig. 1).

DISCUSSION

Hydrazones and their dioxouranium(VI) complexes were synthesised as shown in Fig. 2.

The analytical data for the complexes (Table I) indicate that they have a general formula, $[UO_2L_2X_2]$, where L = AaBH, AaSH, AaINH or AaSCH and X = NO_3^- or CH_3COO^- . All the complexes, except $[UO_2(AaINH)_2(NO_3)_2]$, are non-hygroscopic. They are amorphous powders which are yellow to red in colour and are generally soluble in common organic solvents.







Fig. 2. Synthesis of the Complexes

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Table I

Analytical and Physical Data of the Compounds

S. S.	Compound	Empirical formula	Colour	Decomp. Temp.	Yield %		Found (Cal	culated)%		Molar cor ohm- ¹ cr	iductance 1 ² mol ⁻¹
		(Formula weight)		Ŷ	2	X	υ	Н	z	MeOH	PhNO2
	AaBH	C ₁₇ H ₁₇ O ₂ N ₃ (295)	White	190	65		69.11 (69.15)	5.35 (5.76)	14.18 (14.24)	;	1
5	[UO2(AaBH)2(NO1)2]	UCuHuO:2Ns (984)	Orange	198	70	24.71 (24.19)	42.05 (41.46)	3.71 (3.46)	11.36 (11.38)	<u>5</u> .79	0.75
ŕ	[UO ₂ (AaBH) ₂ (CH ₃ COO) ₂]	UC38H40O10N6 (978)	Yellow	148	70	24.13 (24.34)	46.53 (46.63)	4.25 (4.09)	8.69 (8.59)	5.69	0.86
4.	AaSH	C1,H1,O3N3 (311)	White	178	75	ł	65.89 (65.39)	5.23 (5.47)	13.47 (13.50)	ł	1
പ	[UO2(AaSH)2(NO3)2]	UСыНыО ₁₄ N ₈ (1016)	Yellow	203	80	23.81 (23.43)	40.85 (40.16)	3.43 (3.35)	11.23 (11.02)	7.63	2.38
6.	[UO2(AaSH1)2(CH-COO)2]	UC34H40O12N6 (1010)	Orange	238	78	23.19 (23.56)	44 .75 (45.15)	4.06 (3.96)	8.47 (8.32)	4.59	2.16
7.	AalNH	CI ₅ H16O2N4 (296)	Yellow	168	58	ł	65.11 (64.86)	5.48 (5.41)	18.71 (18.92)	;	1
αÔ	[UO2(AaINH)2(NO3)2]	UC32H32O12N10 (986)	Red	128	75	24.63 (24.14)	38.50 (38.95)	3.33 (3.25)	14.48 (14.20)	15.83	0.34
9.	[UO ₂ (AalNH) ₂ (CH ₃ COO) ₂]	UC34H36O10N8 (980)	Orange	125	75	24.18 (24.29)	44.11 (44.08)	3.75 (3.88)	11.53 (11.43)	11.72	0.58
10.	AaSCH	C1;H14O2N4 (234)	White	185	20	ł	56.81 (56.41)	6.02 (5.98)	23.89 (23.93)	1	ł
11.	[UO2(AaSCH)2(NO3)2]	UC22H26O12N10 (862)	Yellow	240	65	27.81 (27.61)	31.12 (30.63)	3.39 (3.25)	16.30 (16.24)	6.77	1.35
12.	[UO ₂ (AaSCH) ₂ (CH ₃ COO) ₂]	UC26H3O30N8 (856)	Yellowish brown	187	89	27.31 (27.80)	35.88 (36.45)	4.08 (3.97)	13.19 (13.08)	10.76	1.57

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The molar conductance values (Table I) in methanol indicate a certain amount (about 5%) of dissociation of the complexes which may be due to partial replacement of solvent molecules for the coordinated nitrate or acetate groups in solution. The values are too low to include these complexes in the category of even 1:1 electrolytes. However, molar conductance measurements in nitrobenzene conclusively prove the non-electrolytic nature of the complexes which in turn indicates the coordinated nature of the nitrate and acetate groups⁵.

Room temperature magnetic measurements indicate that the complexes are diamagnetic. This is generally expected for $5f^{O}$ UO₂(VI) compounds which are characterized by a spin-paired electronic configuration.

The important electronic spectral bands of the ligands and the complexes are observed in the regions 200-250 and 350-400 nm. They may be attributed, respectively, to $\pi - \pi^*$ and n- π^* type intraligand charge-transfer tranistions. In the spectra of the complexes, additional bands are observed in the region 420-450 nm. They may be assigned to $1 \leq_{g^+} ---> 3_{\pi u}$ for the first excited state of the uranyl absorption and also to the charge-transfer bands arising from the ligand orbital to the 5f or 6d orbitals of uranium. These ligand-metal transitions are strongly affected by the nature of the complexes and are responsible for their bright colour^{6,7}.

The IR assignments for the important bands of the ligands and the complexes are given in Table II. The bands

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Table II

Major IR Absorption Bands for the Ligands and Complexes (cm⁻¹)

Sr. No.	Compounds	v(C=O) (Amide I)	v(C=O) (Hydrazide)	v(C=N)	(N-N)^	v(O=U=O)	(YON)	v(CH ₁ COO)	Amide II, III	
	AaBH	1680 s	1660 s	1660 s	960 s	:			1540 s, 1310 s, 1235 s	
N	[UO ₂ (AaBH) ₂ (NO ₃)2]	1655 s	1658 s	1570 s	985 sh	940 s	1020 s 1435 s 1275 m	;	1544 s, 1300 m, 1245 s	
Ś	[UO2(AaBH));(CH3COO)2]	1660 s	1662 s	1568 s	975 s	938 s		1610 m 1340 m	1548 s, 1310 m, 1220 s	
4	AaSH	1680 s	1650 s	1590 s	970 s	١	ł	1	1548 s, 1328 s	
ы.	[UO2(AaSH)2(NO3)2]	1652 s	1648 s	1553 s	985 s	950 s	1000 s 1425 s 1260 m	ï	1533 s,(sh) 1230 s	
Ų.	[UO2(AaSH)2(CH,COO)2]	1655 s	1655 s	1550 s	980 s	940 s	I	1600 m 1330 m	1545 m, 1230 s	
7.	AalNH	1685 s	1658 s	1595 s	968 s	;	ł	;	1548 s, 1328 m, 1245 s	
σċ	[UO2(AalNH)2(NO3)2]	1655 s	1660 s	1565 s	970 s	955 s	1025 s 1420 s 1265 m	ł	1550 s, 1325 s	
9.	[UO2(AalNH)2(CH3COO)2]	1650 s	1655 s	1560 s	978 s	951 s	I	1610 m 1345 s	1545, 1310 s	
10.	AaSCH	1750 s	1660 s	1610 s	s 066	ł	;	I	1600 m, 1548 s, 1325 s	
11.	[UO2(AaSCH)2(NO:)2]	1685 s	1660 s	1575 s	985 s	945 s	1029 m 1430 s 1268 s	I	1600 m, 1542 s, 1315 s	
12.	[UO ₂ (AaSCH) ₂ (CH ₃ COO) ₂]	1675 s	1657 s	1570 \$	985 s	935 s	i	1600 s 1348 s	1540 s, 1325 s	
S I S	trong; m = medium; sh = should	der.								

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observed around 3480, 3390, 3360,3255 and 3090 cm^{-1} may be attributed to the N-H stretching vibrations. Of these, the two higher frequency ones are prominent in the case of semicarbazone which may be due to the symmetric N-H vibrations of the terminal NH₂ group.

In the spectra of hydrazones, the bands at 1680 and 1620, 1530, 1310 and 1235 cm⁻¹ may be assigned, respectively, to the amide I, II and III frequencies of the anilide group^8 . However, the amide I band of AaSCH is observed at 1750 cm⁻¹. In the spectra of the complexes, the amide I bands shift by an appreciable amount to the lower frequency region, indicating the participation of this carbonyl oxygen in coordination. The amide II and III bands are observed more or less in the same region as in the spectrum of their respective ligands. Bands of strong intensities around 1640-1660 cm⁻¹ in the spectra of the above ligands may be attributed to the carbonyl stretching vibrations of the same position in the spectra of the complexes.

The azomethine stretching modes in the spectra of all the ligands are observed around 1590-1610 cm^{-1} . A shift of this band to 1550-1575 cm^{-1} in the spectra of the complexes demonstrates the participation of the azomethine nitrogen in coordination.

In the spectra of salicyloylhydrazone and its complexes broad bands at 3520 cm^{-1} may be attributed to the O-H stretching mode of the phenolic group. This also confirms

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its non-participation in coordination. In the spectra of the ligands and the complexes, the band due to $\sqrt{(N-N)}$ is observed in the range 960-990 cm⁻¹.

A band of medium to strong intensity in the spectra of the complexes around 935-955 cm⁻¹ may be assigned to V_{as} (O-U-O). The absence of any other V_s (O-U-O) mode suggests that the linearity of this group is conserved in the complexes and hence the two oxygen atoms in the UO₂²⁺ ion are in trans-orientation in the complexes⁹.

In the spectra of the complexes of uranyl nitrate, the bands of strong intensities around 1000-1030 cm⁻¹ may be assigned to the coordinated nitrate groups¹⁰. This is supported by the appearance of two bands in the region 1420-1435 (V_4) and 1260-1275 cm⁻¹ (V_1). From the separation of the V_1 and V_4 modes ($\Delta V \simeq 150$ cm⁻¹) it appears that the nitrate anions are acting as monodentate ligands in all these complexes¹¹.

The bands at 1600-1610 and 1330-1350 cm⁻¹ in the spectra of the complexes of uranyl acetate may be assigned respectively, to $V_{as}(COO^-)$ and $V_{s}(COO^-)$ of the coordinated acetate anions. The large separation between these two bands ($\Delta V \simeq 260 \text{ cm}^{-1}$) demonstrates their coordination in a unidentate fashion¹¹.

Thus, the hydrazones and semicarbazone are found to act as neutral bidentate ligands coordinating through O and N atoms. This is supported by the bands due to (M-O) and (M-

N) stretching vibrations observed around 500-530 and 400-480 $\rm cm^{-1}$, respectively. A coordination number of eight is created around the U(VI) ion by two neutral bidentate ligands, two unidentate anionic ligands (nitrate or acetate) and the two oxygen atoms on the oxocation (Fig. 3).

EXPERIMENTAL

General Information

Uranyl nitrate and acetate were of BDH Analar quality. Acetoacetanilide, isonicotinoylhydrazine and semicarbazide hydrochloride were purchased from Merck. Benzoyl- and salicyloylhydrazines were prepared from the methyl- or ethyl esters of the respective acid and hydrazine hydrate¹². The solvents used for the synthesis and recrystallisation were commercially available ones and were purified by standard methods¹³.

Synthesis of Ligands

The three hydrazones, AaBH, AaSH and AaINH, were prepared by this general procedure. An ethanolic solution of acetoacetanilide (0.89 g, 0.005 mol in 20 mL) was added to a refluxing solution of the respective aroylhydrazine in ethanol (0.68 g of benzoylhydrazine, 0.76 g of salicyloylhydrazine or 0.62 g of isonicotinoylhydrazine, 0.005 mol in 20 mL) and a few drops of dilute HCl. The mixture was maintained at the refluxing temperature for 2 h. Slow evaporation gave the solid product. AaSCH was prepared



Fig. 3. Suggested Structure of the Complexes

as follows: To a solution of semicarbazide hydrochloride (1.11 g, 0.01 mol) and sodium acetate trihydrate (1.36 g, 0.01 mol) in the minimum amount of water (\simeq 15 mL), acetoacetanilide in ethanol (1.77 g, 0.01 mol in 20 mL) was added with vigorous stirring. The mixture was stirred for 2-3 h. The precipitated compound was filtered off, washed with water and dried under reduced pressure over phosphorus(V) oxide.

Preparation of Complexes

The complexes were prepared by following a general method. Methanolic solutions of the ligand (2.95 g of AaBH,

3.11 g of AaSH, 2.96 g of AaINH or 2.34 g of AaSCH, 0.01 mol in 15 mL) and uranyl salt [2.51 g of $UO_2(NO_3)_26H_2O$ or 2.12 g of UO₂(CH₃COO)₂2H₂O, 0.005 mol in 10 mL] were mixed and refluxed for 4-5 h. It was observed that a slight excess of the ligand from the 2:1 molar ratio was useful in most cases [UO2(AaSH)2(NO3)2] precipitated while for better yields. refluxing the reaction mixture. However, the others were isolated as follows. The reaction mixtures, after refluxing for 4-5 h, were concentrated by evaporation until semisolid They were then thoroughly washed residues were obtained. several times with petroleum ether, each time decanting the supernatant liquid, until the solid complexes separated out. They were filtered, washd with methanol and petroleum ether and dried under reduced pressure over phosphorus(V) oxide.

Analyses

The ligands and the complexes were analysed for carbon, hydrogen and nitrogen using a Heraeus CHN-O rapid analyser. Uranium present in the complexes was determined by a standard procedure¹⁴.

Physical Measurements

The molar conductance measurements of the complexes were made in methanol and nitrobenzene using a Biochem conductivity bridge type M-70 and a dip-type cell (cell constant = 0.70 cm⁻¹). Magnetic measurements were carried out using a Gouy-type magnetic balance with $Hg[Co(NCS)_4]$ as the calibrant. Electronic spectra, in the range 200-900 nm, were recorded in the solid state (Nujol mulls), following the procedure recommended by Venanzi¹⁵, on a Hitachi 3200 spectrophotometer. The IR spectra of the ligands and the complexes in the 200-4000 cm⁻¹ region were recorded using KBr discs on a Perkin-Elmer 580 spectrophotometer.

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