Synthesis & Characterization of Nitrato & Acetato Complexes of Dioxouranium(VI) with Disalicylaldehyde Acyl Hydrazones

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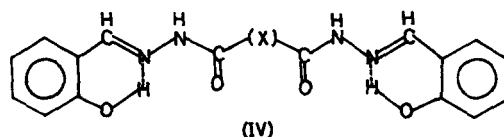Dioxouranium(VI) complexes of disalicylaldehyde oxaloyldihydrazone (H_4A_2), malonoyldihydrazone (H_4B_2), succinoyldihydrazone (H_4C_2), glutaroyldihydrazone (H_4D_2), adipoyldihydrazone (H_4E_2) and phthaloyldihydrazone (H_4F_2) have been synthesized from the reaction of uranyl nitrate hexahydrate and uranyl acetate dihydrate with the title ligands in alcoholic medium. The complexes have the compositions $[(UO_2)_2(H_2L_2)(H_2O)_4(NO_3)_2].2H_2O$ and $[(UO_2)_2(H_2L_2)(C_2H_5OH)_2(CH_3COO)_2].C_2H_5OH$ where $H_4L_2 = H_4A_2$, H_4B_2, H_4C_2, H_4D_2, H_4E_2 and H_4F_2. The complexes have been characterized on the basis of elemental analyses, TGA, DTA, molar conductance, infrared and Raman spectral data.

Metal complexes of acylhydrazones have received great attention during recent years because of their pharmacological applications[1,2], unusual magnetic properties and diverse structural features[3]. Although some complexes of acyldihydrazones with $3d$ metal ions[4-6] and a few of pyridyldihydrazone complexes with actinides[7] have been reported, those of acyldihydrazones with actinides are almost non-existent. This is probably due to the fact that in dihydrazones two hydrazone units are joined together through methylene chains of varying length or phenyl or pyridyl group making the system more complex. Dihydrazones, which react in keto (I), keto-enol (II) and enol (III) forms depending upon the mode of preparation of the complexes, nature of the solvent, the pH of the reaction medium, the nature of metal salt and the molar ratio of the reactants, give rise to polymeric complexes through both ligand bridging (because of their flexibility) and oxo-bridging.
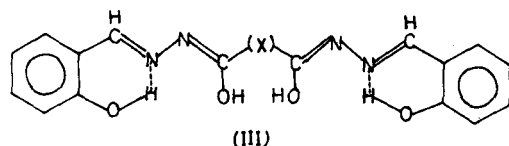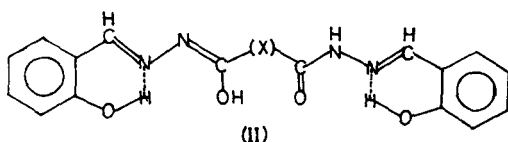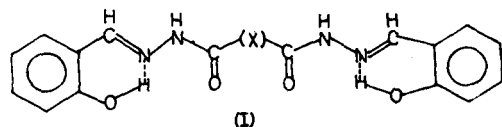
We report here the preparation and characterization of dioxouranium(VI) complexes with some disalicylaldehyde acylhydrazones (IV).

(IV)

$X = -(CH_2)_n -$

n	H_4L_2	Ligand
0	H_4A_2	Disalicylaldehyde oxaloyldihydrazone
1	H_4B_2	Disalicylaldehyde malonoyldihydrazone
2	H_4C_2	Disalicylaldehyde succinoyldihydrazone
3	H_4D_2	Disalicylaldehyde glutaroyldihydrazone
4	H_4E_2	Disalicylaldehyde adipoyldihydrazone

$X = -C_6H_4 - H_4F_2$ Disalicylaldehyde phthaloyldihydrazone

Materials and Methods

Uranyl nitrate hexahydrate, uranyl acetate dihydrate, diethyl esters of oxalic, malonic, succinic, glutaric, adipic and phthalic acids, hydrazine hydrate and salicylaldehyde were BDH reagents of AR or equivalent grade. Acyldihydrazines, viz., oxaloyl, malonoyl, succinoyl, glutaroyl, adipoyl and phthaloyl dihydrazines were prepared by reacting the corresponding diethyl esters (1 mol) with hydrazine hydrate (2 mol). The dihydrazones were prepared by reacting warm or refluxing dilute solutions of the above acid dihydrazides (1 mol) with salicylaldehyde (2 mol) and were collected as described elsewhere[8].

Uranium in the complexes was determined by standard literature method[9]. The ligands in the complexes were determined in 5M H_2SO_4 with standard $KMnO_4$ using a calibration curve[5]. Ni-

(I)

(II)

(III)

trogen was determined by microanalytical method. Nitrate was determined as nitron nitrate. Water and ethanol contents were determined by heating the samples in an electric oven maintained at 80 and 180°C and estimating the loss in weight. The IR spectra were recorded in KBr in the range 4000-180 cm^{-1} on a Perkin-Elmer-983 spectrophotometer. Raman spectra of $(UO_2)_2(H_2A_2)(NO_3)_2$-$6H_2O$ and $(UO_2)_2(H_2A_2)(CH_3COO)_2 3C_2H_5OH$ complexes were recorded on a Raman spectrophotometer (Ramalog 1403) using rotating sample technique in order to avoid the decomposition of the samples. The molar conductances of the complexes at 10^{-3} M dilution in ethanol and DMF were measured using an Elico conductivity cell. Thermal studies of the complexes were carried out in an atmosphere of air, under static conditions, heating the specimen at the rate of 10°C/min in the range 0-800°C, using heated alumina as the standard reference material.

Preparation of the complexes

The following general procedures were used for the isolation of the complexes:

(i) Uranyl nitrate hexahydrate (0.1 M) was dissolved in ethanol. The ligand (2 g), powdered well in an agate morter, was taken in 50 ml ethanol and stirred well to get a homogeneous slurry. Uranyl nitrate solution was added to the ligand slurry with gentle stirring maintaining the metal: ligand molar ratio 3:1. The mixture was refluxed for 2 hr. In the case of H_4A_2 and H_4F_2, the complexes precipitated immediately but in the cases of other ligands, a solution was obtained. The solution, on concentration (~ 70 ml) followed by addition of ether, precipitated a semi-solid. This was extracted with benzene and stirred well for about half an hour and kept overnight. The complex so obtained was washed with ethanol-benzene mixture, benzene and dried over anhydrous calcium chloride.

(ii) Uranyl acetate dihydrate was dissolved in ethanol containing one drop of acetic acid to get a 0.1 M solution. Any undissolved material was filtered off. Uranyl acetate solution was added to the ligand slurry (2 g) obtained as above with gentle stirring maintaining the metal:ligand molar ratio at 3:1. The mixed solution, after refluxing for one hour, precipitated the complex which was isolated as above.

Results and Discussion

The results of elemental analyses (Table 1) are consistent with 2:1 (metal:ligand) stoichiometry and accordingly, the general formulae $(UO_2)_2(H_2L_2)(NO_3)_2$ $6H_2O$ and $(UO_2)_2(H_2L_2)(CH_3COO)_2 3C_2H_5OH$. All the complexes are amorphous powders and their colours vary from dull yellow, yellow, dull orange,

Table 1—Analytical and Melting Point Data of Dioxouranium(VI) Complexes of Acyldihydrazones

Sl. No.	Complex	Colour (m.p./d.p., °C)	Found (Calc.) %				
			U	N	Ligand	NO$_3$	H$_2$O/C$_2$H$_5$OH
1	$(UO_2)_2(H_2A_2)(NO_3)_2 6H_2O$	Brown (> 250*)	43.01 (43.43)	7.47 (7.66)	29.51 (29.56)	10.97 (11.31)	9.97 (9.85)
2	$(UO_2)_2(H_2A_2)$ $(CH_3COO)_2 3C_2H_5OH$	Brown (> 250*)	42.82 (42.50)	3.11 (3.21)	28.75 (28.93)	—	11.27 (12.32)
3	$(UO_2)_2(H_2B_2)(NO_3)_2 6H_2O$	Red brown (170)	42.69 (42.88)	7.61 (7.57)	30.01 (30.45)	10.98 (11.17)	9.48 (9.78)
4	$(UO_2)_2(H_2B_2)$ $(CH_3COO)_2 3C_2H_5OH$	Brown (> 250)	41.69 (41.98)	4.77 (4.94)	29.99 (29.81)	—	11.97 (12.17)
5	$(UO_2)_2(H_2C_2)(NO_3)_2 6H_2O$	Brown (165)	42.05 (42.35)	7.38 (7.47)	31.09 (31.32)	11.00 (11.03)	9.51 (9.61)
6	$(UO_2)_2(H_2C_2)$ $(CH_3COO)_2 3C_2H_5OH$	Orange (> 250*)	41.87 (41.46)	4.62 (4.88)	30.78 (30.66)	—	11.98 (12.02)
7	$(UO_2)_2(H_2D_2)(NO_3)_2 6H_2O$	Dull orange (160)	42.03 (41.83)	7.29 (7.38)	31.98 (32.16)	10.89 (10.00)	9.18 (9.47)
8	$(UO_2)_2(H_2D_2)$ $(CH_3COO)_2 3C_2H_5OH$	Dark orange (> 250)	40.66 (40.96)	4.93 (4.82)	31.72 (31.50)	—	11.98 (11.88)
9	$(UO_2)_2(H_2E_2)(NO_3)_2 6H_2O$	Orange (185)	41.01 (41.32)	6.98 (7.29)	32.76 (32.99)	10.65 (10.76)	9.29 (9.38)
10	$(UO_2)_2(H_2E_2)$ $(CH_3COO)_2 3C_2H_5OH$	Orange (> 250)	40.07 (40.48)	4.82 (4.76)	31.99 (32.31)	—	11.68 (11.73)
11	$(UO_2)_2(H_2F_2)(NO_3)_2 6H_2O$	Yellow (> 250*)	40.59 (40.61)	7.32 (7.17)	34.00 (34.13)	10.27 (10.58)	9.08 (9.22)
12	$(UO_2)_2(H_2F_2)$ $(CH_3COO)_2 3C_2H_5OH$	Dull yellow (> 250)	39.72 (39.80)	4.49 (4.68)	33.29 (33.44)	—	9.78 (9.87)

*Decompose.

orange, red brown to brown. The nitrato complexes of the ligands $H_4B_2 - H_4E_2$ are partially soluble in ethanol, methanol and acetone and completely so in DMF, but are insoluble in water and other organic solvents like ether, chloroform, carbon tetrachloride and benzene. Acetato complexes of these ligands are soluble in donor solvents like DMF and DMSO only. The nitrato complexes of H_4A_2 and H_4F_2 are only sparingly soluble in DMF and DMSO while acetato complexes are not soluble at all. The molar conductances of the nitrato complexes of H_4B_2 to H_4E_2 ligands lie in the ranges 154-190 and 145-167 ohm^{-1} cm^2 mol^{-1} in methanol and DMF respectively indicating their 1:2 electrolytic behaviour[10]. Such high values of molar conductances are due to solvolysis of the complexes in coordinating solvents, methanol and DMF[11]. The molar conductance values (4.9 to 15.5 ohm^{-1} cm^2 mol^{-1}) of acetato complexes indicate their non-electrolytic nature in DMF[10]. This is, most probably, due to strong coordination by acetato group.

The nitrato and acetato complexes show mass loss corresponding to two water and one ethanol molecules at 80°C indicating their lattice-held nature. The complexes show mass loss corresponding to four water and two ethanol molecules at 180°C indicating their coordinated nature. In the nitrato complexes of H_4B_2 to H_4E_2, we could get satisfactory results by heating the samples although they started melting. The TGA curve of the acetato complex No. 6 (see Table 1 for numbering) shows mass loss corresponding to three ethanol molecules in the temperature range 70-160°C after which the complex remains stable up to 300°C. The DTA curve of the acetato complex shows a broad endothermic peak in the region 70-220°C with a minimum at 160°C giving additional evidence for the presence of ethanol molecules. The loss of one ethanol molecule in the temperature range 70-120°C indicates that it is held in the lattice while the loss of two ethanol molecules in the temperature range 120-160°C indicates that they are coordinated to the uranyl ion. The complex starts decomposing beyond 300°C and attains stability in weight after 550°C indicating the formation of U_3O_8. DTA curve shows that the complex decomposes in two distinct steps, losing two CH_3CO and two $-N_2HCOCH_2$ groups in the range 300-380°C and two phenyl rings in the range 380-550°C. Compared to acetato complex (No. 6), the nitrato complex (No. 5) gives no indication of its stability at any stage once the decomposition has commenced after loss of coordinated water molecules upto 250°C. The decomposition of the complex starts after 250°C and two exothermic peaks are observed in the temperature ranges 250-380 and 380-630°C. The TGA curve shows loss of weight corresponding to two and four water molecules in the temperature ranges

70-120°C and 120-250°C respectively. DTA curve shows one endothermic peak from 70 to 120°C and another between 120 and 250°C corresponding to lattice held and coordinated water molecules respectively. The complex decomposes above 250°C and shows maxima at 335 and 445°C in the ranges 250 to 380°C and 380 to 630°C which corresponds to loss of two nitro and two $-N_2HCOCH_2 -$ groups and two phenyl groups, respectively.

The IR spectra of the ligands show bands due to amide I and $C = N$ stretching vibrations in the 1700-1600 cm^{-1} region. Recently, Paolucci, et al.[7] have reported the existence of tautomeric keto-enol phenomenon in the solid state in dihydrazones of pyridine dicarboxylic acid on the basis of the presence of two bands at ~ 1700 and 1685 cm^{-1} in their IR spectra. In the present study, we have observed only one band at 1666 cm^{-1} in the spectrum of H_4E_2 and at 1655 cm^{-1} in H_4F_2 while in the other ligands two bands at ~ 1674 and 1666 cm^{-1} are observed. The presence of bands in the 1674-1655 cm^{-1} region rules out the possibility of the existence of tautomeric keto-enol equilibria in ligands and suggests that the ligands exist primarily in the keto form. The positions of the bands indicate the involvement of intermolecular and intramolecular hydrogen bonding. The appearance of amide I band at as low position as 1655 cm^{-1} indicates that the hydrogen bonding is stronger in H_4F_2 than that in the other ligands which is also confirmed by the appearance of νOH and νNH bands at as low positions as 3149 cm^{-1}.

The amide I bands of the complexes 1, 3, 6 and 8 show a negative shift of 12-51 cm^{-1} and appear as medium to strong bands in the 1662-1621 cm^{-1} region indicating coordination of the ligand through $> C = O$ group to the uranyl ion. However, the IR spectra of the other complexes in the region 1700-1600 cm^{-1} are difficult to interpret due to weakening of amide I band and negative shift by about 50-60 cm^{-1} in $\nu C = O$ mode. As a result, amide I band either appears as a shoulder to the $\nu C = N$ band or merges with it. Similar observations have been made by Iskander et al.[6] in the copper(II) and nickel(II) complexes of some acyldihydrazone ligands. Such a negative shift and weakening of amide I band may be attributed to strong bonding between oxygen of carbonyl group and uranyl ion. The complexes show bands in the 1590-1500 cm^{-1} region which may be due to $\nu C - O$ and amide II modes. The bands in the region 1573-1552 cm^{-1} in the IR spectra of the ligands undergo splitting and suffer positive as well as negative shifts on complex formation and appear in the 1590-1564 cm^{-1} and 1550-1520 cm^{-1} regions respectively. The bands in the 1550-1520 cm^{-1} region are due to the negative shift of amide II band by 2-55 cm^{-1} and the coordination of $> C = O$ group to the uranyl ion suggesting the exist-

Table 2—Important Spectral Bands of Acyldihydrazones and Their Dioxouranium(VI) Complexes

S. No.	Ligand/Complex	$\nu C = O$	$\nu C = N$	Amide II + $\nu(C-O)$ (phenyl)	$\nu(C-O)$	Anion vibrations
	H_4A_2	1674s 1666s	1624s	1572s 1525s	1271s	—
	H_4B_2	1673s 1666s	1623s 1612s	1572s 1553s	1269s	—
	H_4C_2	1673s 1666s	1623s	1572s	1270s	—
	H_4D_2	1673s 1666s	1623s 1609s	1552s	1275s	—
	H_4E_2	1666s	1623s 1612s	1555s	1278s 1261m	—
	H_4F_2	1655s	1623s 1612s	1573s 1554s	1279s 1265s	—
1	$(UO_2)_2(H_2A_2)(NO_3)_2$ $6H_2O$	1662m	1603m	1564s 1542m	1305m 1261w	1384s, 821w, 1746w
2	$(UO_2)_2(H_2A_2)$ $(CH_3COO)_23C_2H_5OH$	—	1605s	1590s 1542s	1306m 1273w	1554s, 1411w
3	$(UO_2)_2(H_2B_2)(NO_3)_2$ $6H_2O$	1621s	1583s	1572s 1547s 1530s	1314m 1273m	1383s, 825w, 1709s
4	$(UO_2)_2(H_2B_2)$ $(CH_3COO)_23C_2H_5OH$	—	1605s	1564s 1537s	1307m	1547s, 1409m
5	$(UO_2)_2(H_2C_2)(NO_3)_2$ $6H_2O$	—	1601s	1550s	1283s	1384s, 853w, 1780w
6	$(UO_2)_2(H_2C_2)(NO_3)_2$ $(CH_3COO)_23C_2H_5OH$	1653m	1602s	1574m 1541w	11307w	1547m**, 1394m
7	$(UO_2)_2(H_2D_2)(NO_3)_2$ $6H_2O$	—	1602s	1588m 1550m	1283m	1384s, 825w, 1761w
8	$(UO_2)_2(H_2D_2)$ $(CH_3COO)_23C_2H_5OH$	1657m	1610s	1566s	1306m 1268m	1566s**, 1401m
9	$(UO_2)_2(H_2E_2)(NO_3)_2$ $6H_2O$	—	1602s	1566m 1550m	1282s	1384vs, 840w, 1767w
10	$(UO_2)_2(H_2E_2)$ $(CH_3COO)_23C_2H_5OH$	—	1606s	1564s 1542s	1305m	1564s**,1395m
11	$(UO_2)_2(H_2F_2)(NO_3)_2$ $6H_2O$	—	1628s	1570s 1520m	1262m	1391vs, 826w*, 1702w
12	$(UO_2)_2(H_2F_2)$ $(CH_3COO)_23C_2H_5OH$	—	1631s	1569s	1262m	1569s**, 1391s

*Masks ligands bands; **overlaps with the $C-O$ or amide II band of the ligand.

ence of the ligands in the keto form(I) in the complexes. The $\nu C - O$ band is present in the region 1590-1564 cm^{-1} signifying a positive shift by about 11-35 cm^{-1}. Such high shift of $\nu C - O$ band is considered diagnostic of binuclear or polynuclear complexes through oxobridging. The multiplicity of the $\nu C = N$ bands (1624-1609 cm^{-1}) exhibited in the IR spectra of the ligand is lost upon complexation. Further, they suffer negative shift by about 10-40 cm^{-1} in all the complexes except in those of H_4F_2 complexes. The negative shift of $\nu C = N$ band is attributed to a decrease in the π-bond character of the $>C = N$ group as a result of nitrogen to metal coordination.
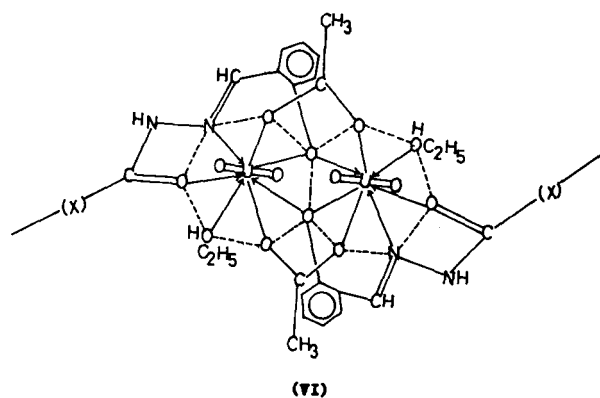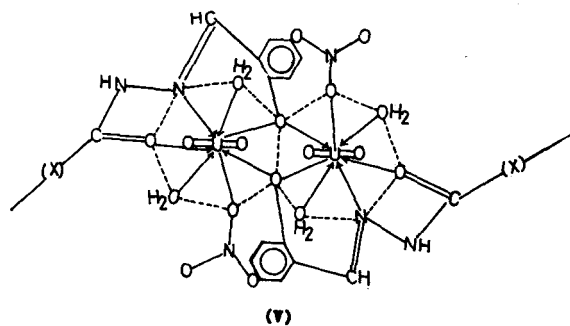
However, the IR spectra of the phthalamido complexes show a positive shift in the $\nu C = N$ mode. This fact can be understood in terms of the drainage of the electron density, attributed to the replacement of methylene groups by phenyl group between two hydrazone units, from the phenyl ring of salicylaldimine group to the uranyl ion through the azine group nitrogen atom increasing carbon and nitrogen bond order as has been reported in thiosemicarbazonato complexes[12]. In other complexes the drainage of π-electron density occurs through oxygen atoms. From the above discussion, it is evident that the ligands act as dibasic hexadentate and bond to uranyl ion through phenolic oxygen, carbonyl oxygen and azine group nitrogen. On examining the spectra of the ligands and their complexes below 600 cm^{-1}, the new bands appearing in the ranges 590-497, 496-421 and 413-300

cm^{-1} are tentatively assigned to $\nu(U-O)$ (phenolic), $\nu(U-O)$ (carbonyl) and $\nu(U-N)$ respectively.

The IR spectra of all the uranyl complexes studied here show strong absorption in the region 938-907 cm^{-1} masking weak to medium ligand bands and weak to medium to strong absorption in the 871-851 cm^{-1} region respectively assigned to ν_3 and ν_1 vibrations of the uranyl group. In uranyl complexes $(UO_2)_2$ (H_2L_2) $(NO_3)_2$ $6H_2O$ and $(UO_2)_2$ (H_2L_2) $(CH_3COO)_2$ $3C_2H_5OH$ (where $H_4L_2 = H_4C_2$, H_4E_2) the assignment of ν_1 is a little doubtful as bands of weak to medium intensity occur in the IR spectra of the uncoordinated ligands also in the 864-853 cm^{-1} region. However, H_4F_2 complexes show a strong band at ~855 cm^{-1} which can not be assigned to ligand bands. The forbidden vibrations may become allowed as a result of particular symmetry of the ligand field around uranyl group in the complexes rather than slight bending of this group. The ν_3 band in some complexes (Table 2) is resolved into a doublet[7,13-15]. The Raman spectra of the complexes $(UO_2)_2$ (H_2A_2) $(NO_3)_2$ $6H_2O$ and $(UO_2)_2$ (H_2A_2) $(CH_3COO)_2$ $3C_2H_5OH$ in the range 1000-800 cm^{-1} show a strong band centred at 864 and 860 cm^{-1} respectively, but do not show band corresponding to ν_3. The doubly degenerate OUO bending mode is observed as a medium to strong band in the 245-212 cm^{-1} region and it masks the ligand bands occurring in this region.

The IR spectra of the acetato complexes show $\nu_s COO$ mode in the region 1412-1391 cm^{-1} and $\nu_{as} COO$ mode at 1564-1547 cm^{-1}; but in some complexes the latter band is masked by either amide II or $\nu C-O$ band. The positions of the COO bands are in agreement with the bidentate coordination of acetato group with uranyl ion. Keeping in view the difference between the solubility, decomposition temperature (melting point) of the nitrato and acetato complexes and the separation (180-138 cm^{-1}) between $\nu_{as} COO$ and $\nu_s COO$ modes, the bridging nature of the acetato groups is more probable in the present complexes[16]. The IR spectra of the nitrato complexes show a strong band in the region 1392-1384 cm^{-1} (masking ligand band) and a weak band in the region 853-821 cm^{-1} suggesting that nitrato group is present either in ionic or weakly coordinated form[18]. The IR spectra of the nitrato complexes in the region 1800-1700 cm^{-1} show combination bands (diagnostic of the type of nitrato group present). A single band attributable to $(\nu_1 + \nu_4)$ mode is observed which indicates that strong coordination by nitrato group is unlikely[17]. Considering the compositions of the complexes, their solubility behaviour in the common organic solvents, high melting points/decomposition points, the dibasic hexadentate nature of the ligand and the presence of oxo and ligand bridging, both the nitrato and acetato dioxouranium(VI) complexes may tentatively be assigned oxo-bridged polymeric structures (V and VI) involving nine coordinate uranium atom.

(V)

(VI)

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