Polymeric Dioxouranium(VI) Complexes with Acyldihydrazones

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Abstract

Dioxouranium(VI) complexes of disalicylaldimine oxamide (H_4A), malonamide, (H_4B), succinamide (H_4C), glutaramide (H_4D), adipamide (H_4E), and phthalamide (H_4F) have been synthesized in aqueous alcoholic media and characterized by elemental analyses, decomposition temperature, thermoanalytical data, molar conductances, infrared and Raman spectral data. The complexes conform to composition $(UO_2)_2(L) \cdot 6H_2O$ (where $H_4L = H_4A$, H_4B, H_4C, H_4D, H_4E, H_4F). The infrared spectral data indicate that the ligands coordinate to the uranyl group in the enol form through enolized carbonyl oxygen, azine group nitrogen and phenolic oxygen, and suggest that the ligands function as tetrabasic hexadentate ligands. The position of the phenolic oxygen group is diagnostic of the presence of an oxo-bridge. Polymerization arises through ligands as well as oxo-bridging. The infrared and Raman spectra indicate that the linearity of the UO_2^{2+} group is maintained in all these complexes with the ligand atoms arranged in the equatorial plane perpendicular to the linear uranyl group. It has been found that all the complexes show only one band due to asymmetric stretching vibration of the uranyl group, indicating the same coordination environment around the uranium atom in the complexes and thus suggesting that the two hydrazone parts of the ligands are attached to different uranyl groups in a symmetrical linear fashion. Further it has been observed that the asymmetric stretching frequency of the uranyl group decreases with an increase in the number of methylene groups between the two C=O groups. From this the effect of increasing the number of methylene groups on the coupling between two C=O groups has been discussed. It has been found that the phenyl ring in the phthalamide complex shows electron-withdrawing capacity on the phenyl group of the two salicylaldiminato units.

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Introduction

There has been a considerable amount of interest in the chemistry of hydrazones because of their potential pharmacological applications [1–4]. Metal complexes of monoacyl- and aroyl-hydrazones have been reported [11–14]. In such studies hydrazones have been shown to exhibit keto–enol tautomerism. In particular, hydrazones derived from *o*-hydroxy aromatic aldehydes and ketones and a variety of acid hydrazides give rise to condensed systems *i.e.* bi- and polynuclear complexes involving bridging via phenolic oxygen atoms. The formation of bi- and polynuclear complexes, which are of interest because of their unique biochemical properties and their analytical and technological potential [7–10], possess interesting properties depending, among other things, on the shape of the ligand and the nature of its donor atoms. Although metal complexes of monoacyl and aroyl hydrazones have been studied in greater details [11–14], those of acyldihydrazones have received much less attention [15–17]. In such studies, dihydrazones have been shown to enolize to different extents depending upon the mode of the preparation of the complexes, the nature of the reaction medium, the pH of the reaction medium, the metal salt and the molar ratio of the metal salt and the ligand used. They give rise to polymeric complexes through both the ligand as well as oxo-bridging because of their flexibility in three-dimensional space. The ligands derived from the condensation of salicylaldehyde and acyldihydrazines possess eight donor sites and can offer any set of donor atoms depending upon the preferred stereochemical disposition of the metal valences and the nature of the bonds formed in the coordination processes. The metal complexes of acyl- and aroyl-dihydrazones need further investigation in order to have a thorough understanding of their complexation behaviour. Because of the complex chemistry of the uranyl group and its tendency to coordinate from 4 up to 8 atoms in an equatorial plane [31, 32], it appeared especially suitable to explore the mode of coordination of the octadentate

ligands of the type **I**, in which two hydrazone moieties are joined together through alkyl chains of varied lengths. In particular, it was of interest to investigate how the tendency of these dihydrazones to act as bridging or fused polynucleating ligands might be influenced by the length and point of attachment of the connecting alkyl chains.

The present study of the preparation, infrared and Raman spectral features of the coordination compounds formed by the interaction of uranyl acetate with ligands was, therefore, undertaken to elucidate: the form in which the ligands coordinate to the uranyl group; the possible coordination arrangement of the donor groups around the uranyl group; whether the ligands coordinate to the same metal ion leading to monomeric complexes; the effect of increasing the number of methylene or phenyl groups between two hydrazone units on the uranyl group frequencies; the effect of the complexation on the coupling of the two C=O vibrations either in keto form or in the enolic form; and also the effect of the replacement of methyl groups by the phenyl group on complexation.
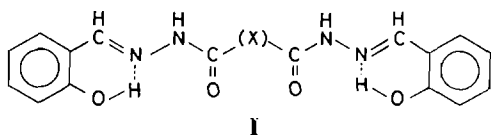

I

Fig. 1. X = $-(CH_2)_n-$

n	H₄L	
0	H₄A	Disalicylaldimine oxamide
1	H₄B	Disalicylaldimine malonamide
2	H₄C	Disalicylaldimine succinamide
3	H₄D	Disalicylaldimine glutaramide
4	H₄E	Disalicylaldimine adipamide
X = $-C_6H_4-$	H₄F	Disalicylaldimine phthalamide

Experimental

Materials and Measurements

Uranyl acetate dihydrate, diethyl esters of oxalic, malonic, succinic, glutaric, adipic and phthalic acids, hydrazine hydrate and salicylaldehyde were of BDH, AR or equivalent grade. The organic acid dihydrazides, *viz.* oxalic, malonic, succinic, glutaric, adipic and phthalic acid dihydrazides, were prepared by reacting the diethyl esters (1 mol) with hydrazine hydrate (2 mol). The dihydrazones were prepared by reacting **warm** or refluxing dilute ethanol solutions of the above acid hydrazides (1 mol) with salicylaldehyde (2 mol). All the ligands were suction filtered, washed with water and ethanol and dried at 70 °C in an electric oven and characterized as described elsewhere [33].

Preparation of the Complexes

As the methods of syntheses of all the uranyl complexes are similar, only a representative method is described. Disalicylaldimine oxamide was powered well in an agate morter and placed in a beaker containing a water–ethanol (1:3) mixture and stirred well to give a homogeneous slurry. A hot slurry (0.01 M, 50 ml) of the ligand was added to an aqueous uranyl acetate dihydrate solution (0.01 M, 150 ml) with gentle stirring. The precipitation of the complexes started in the cold. The reaction mixture was refluxed for about 1 h over a steam bath to complete the reaction. The complexes were hot filtered by suction, washed with a water–ethanol mixture and then with ether, and were dried over anhydrous calcium chloride in a desiccator.

Elemental Analyses (Table I) and Measurements

Uranium was determined by standard literature procedures [18]. The ligands in the complexes were estimated volumetrically in 5 M H_2SO_4 with standard $KMnO_4$ using a calibration curve [17]. Carbon, hydrogen and nitrogen were estimated by microanalytical methods. A thermogravimetric study of one sample as an example was carried out manually by heating the sample at the rate of 10 °C per min on a TGA unit supplied by the Fertilizer Corporation of India (FCI), Sindri. The molar conductances of the complexes at 10^{-3} M dilution in DMSO were measured using an Elico conductivity bridge model CM-82 T, with a dip type conductivity cell. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr pellets in the 4000–180 cm^{-1} region. The Raman spectrum was recorded on a Raman spectrophotometer (Ramalog 1403) as KBr pellets by employing a rotating sample technique to avoid decomposition of the sample.

Results and Discussion

Because of the presence of eight bonding sites, the ligands can bond to metal ions in several different ways: as a monobasic bidentate ligand coordinating through one hydroxyl oxygen and one azine group nitrogen, as a monobasic tridentate or dibasic tridentate ligand coordinating through one hydroxyl oxygen, one azine group nitrogen and one C=O group while the other half of the molecule remains unbonded; as a neutral bidentate ligand coordinating either through two carbonyl oxygens or the two secondary ammine nitrogen atoms with the OH groups remaining intact hydrogen bonded in the complexes; as a dibasic tetradentate ligand coordinating through the two hydroxyl oxygen and the two azine group nitrogen atoms; and as dibasic hexadentate ligands bonding to the same metal ion through the two hydroxyl oxygens, two azine group nitrogens and

TABLE I. Analytical, Decomposition Data and Molar Conductance Data of Dioxouranium(VI) Complexes of Acyldihydrazones

| Complex | Colour | Decomposition temperature (°C) | Analysis, found (calc.) (%) | | | | | | Λ_m (ohm^{-1} cm^2 mol^{-1}) |
			U	C	H	N	Ligand	H_2O	
$(UO_2)_2(A) \cdot 6H_2O$ (1)	light orange	>300	48.73 (49.07)	19.51 (19.79)	2.31 (2.27)	6.28 (5.77)	33.66 (33.20)	10.82 (11.13)	0.7
$(UO_2)_2(B) \cdot 6H_2O$ (2)	dark orange	>300	48.13 (48.37)	20.24 (20.73)	2.40 (2.44)	5.93 (5.93)	34.33 (34.15)	10.48 (10.98)	1.3
$(UO_2)_2(C) \cdot 6H_2O$ (3)	orange	>300	47.28 (47.69)	21.17 (21.64)	2.67 (2.61)	5.39 (5.61)	35.53 (35.07)	11.32 (10.82)	0.9
$(UO_2)_2(D) \cdot 6H_2O$ (4)	orange	>300	47.39 (47.04)	22.97 (22.53)	2.72 (2.77)	5.81 (5.53)	35.35 (35.97)	11.13 (10.67)	2.1
$(UO_2)_2(E) \cdot 6H_2O$ (5)	dark orange	>300	46.53 (46.39)	23.83 (23.39)	3.01 (2.92)	5.27 (5.46)	36.36 (36.84)	10.89 (10.53)	1.7
$(UO_2)_2(F) \cdot 6H_2O$ (6)	yellow	>300	45.23 (45.51)	25.73 (25.24)	2.45 (2.49)	5.03 (5.35)	38.36 (38.05)	10.02 (10.33)	0.5

two carbonyl oxygens in the keto form. Further, these ligands may undergo enolization affording newer bonding possibilities leading to the formation of the binuclear or polynuclear complexes. All the above possibilities can be actually realized in practice if the metal salt, concentration of metal ion and ligand, reaction medium, pH and temperature are varied.

As only one mode of preparation of the complexes has been used in the present study, the isolated complexes are thought to have similar stoichiometry. The results of elemental analyses are consistent with 2:1 metal to ligand stoichiometry and accordingly these complexes have the general formula $(UO_2)_2(L) \cdot 6H_2O$. The complexes are either dark brownish red, dark red, orange or dull yellow coloured substances and are insoluble in common organic solvents. However, the complexes dissolve in highly coordinating solvents like DMF and DMSO. All the complexes decompose above 300 °C. The electrolytic conductance measurements of these complexes (0.5–2.1 mhos) in DMSO solution indicate their non-electrolytic nature in this solvent.

The absence of anions of original metal salt in the resulting complexes indicates liberation of protons of the –OH group and/or >C–OH group formed from enolization of the C=O group under the buffer action of uranyl acetate and acetic acid in aqueous medium. The solubility and high decomposition temperature indicate the polymeric nature of the complexes in the solid state.

The loss of weight of the complexes was obtained by heating a small amount of sample in a glass tube for 4 h in an electric oven maintained at 100 °C and 180 °C, respectively, and passing the vapours through a trap containing anhydrous copper sulphate (which turned blue). The loss of weight at 100 °C corresponds to the expulsion of two water molecules and at 180 °C to four water molecules. The expulsion of four water molecules at 180 °C indicates that they are coordinated [19] to the uranyl ion. The thermogravimetric study of complex **3** was carried out as a representative sample. The decomposition of the complex occurs in five prominent steps, *i.e.* 80–240, 300–360, 360–540, 540–720 and above 720 °C. The complex loses mass steadily in one step between 80 and 240 °C, the average mass loss being 1.5% at 20 °C temperature intervals; the mass loss corresponds to six water molecules. This step indicates that lattice and coordinated water molecules are lost simultaneously in a single continuous step. The simultaneous loss of lattice and coordinated water molecules may, most probably, be due to the hydrogen bond network that permeates the lattice. The hydrogen bonding may be between the lattice-held water molecules and coordinated water molecules. When there is a simultaneous loss of lattice and coordinated water molecules in a single step, then caution must be exercised in the

classification of water as lattice or coordinated on the basis of TGA alone, unless confirmed by crystallographic studies. However, on the basis of loss of mass at 180 and 100 °C, we maintain that four water molecules are coordinated to the uranium and two water molecules are held in the lattice by hydrogen bonding with the coordinated water molecules, but this still remains tentative. After the initial loss of water molecules, the mass of the complex remains almost constant over 240–300 °C, the average mass loss being about 0.5% at 20 °C temperature interval. The significant decomposition of the complex occurs in the 300–360 °C temperature range, the average mass loss being 5% at 20 °C temperature intervals. The mass loss in this temperature range corresponds approximately to two phenyl and two nitrogen groups. The complex decomposes steadily in the temperature ranges 360–540, 540–720 and above 720 °C, the average mass loss being about 1.3, 0.5 and 0.3% at 20 °C temperature intervals until a constant weight is attained above 800 °C.

Partial IR data of the ligands and their uranyl complexes are listed in Table II. Since there are a number of bands arising due to various groups present in the ligand (viz. $>C=O$, $>C=N$, $N-C=O$, $-OH$, $-NH$, phenyl ring, C–N and C–H), which occur in the overlapping regions, it is difficult to assign unambiguously the bands due to various groups and locate their respective positions upon coordination. However, a few significant bands have been selected to observe the effect of coordination on ligand vibrations in the complexes. The assignments of the bands are based on the interpretations advanced for a number of acyl- and aroyl-hydrazones [12–17].

One characteristic feature of the IR spectra of the uranyl complexes presently studied is that they contain less bands than their corresponding parent hydrazone. This fact coupled with the stoichiometry of the complexes indicates that the ligands coordinate symmetrically to metal atoms in the enol form, which is substantiated by the destruction of the amide structure as evident from the disappearance of the absorption bands due to amide groups in the IR spectra of the metal complexes compared to those of the parent ligands.

The ligands show medium to strong broad bands in the 3500–3250 and 3200–3000 cm^{-1} region with multiplet structure with maximum absorption in the 3423–3328 and 3195–3149 cm^{-1} region, which are attributed to the presence of $-OH$ and $-NH$ groups, respectively, each in duplicate. However, H$_4$A shows additional bands at 3278 and 3232 cm^{-1}, and H$_4$F shows a single absorption band at 3149 cm^{-1}. Upon complexation the band in the 3195–3149 cm^{-1} region disappears and a single broad band is observed in the 3500–3100 cm^{-1} region with maximum absorption around 3423 cm^{-1}. The disappearance of

the band in the 3195–3149 cm^{-1} region and appearance of a single broad band in 3500–3100 cm^{-1} region with maximum absorption around 3423 cm^{-1} suggests the enolization of the ligand and presence of coordinated water molecules. The most outstanding feature of the IR spectra of the ligands and their complexes is observable in the 1700–1600 cm^{-1} region which contains bands due to $\nu(C=O)$ and $\nu(C=N)$ stretching vibrations. Recently, Paolucci et al. [16] have studied uranyl complexes of the dihydrazone of pyridine carboxylic acid and have suggested that the dihydrazones exist in the tautomeric keto–enol form in the solid state, based on the presence of two bands at ~1700 and 1685 cm^{-1} in the IR spectra in the solid state. They attributed the band at 1700 cm^{-1} to a keto group of benzenoid structure and the band at 1685 cm^{-1} to a keto group of the hydrazido unit. In the present study we have observed only one band at 1666 cm^{-1} in H$_4$E and 1655 cm^{-1} in H$_4$F, while in the other ligands two bands occur at ~1674 and 1666 cm^{-1}. The presence of a band at 1674–1655 cm^{-1} rules out the possibility of the existence of the tautomeric keto–enol equilibrium in ligands in the solid state. The presence of two bands in the dihydrazones H$_4$A to H$_4$D can be attributed to vibrational coupling between the two C=O groups present in the same molecule. In the cases of H$_4$E and H$_4$F, the two bands overlap with one another giving rise to only one band. These considerations suggest that the ligands primarily exist in the keto form [21]. The position of the bands indicates the involvement of intermolecular and intramolecular hydrogen bonding. The appearance of an amide I band as low as 1655 cm^{-1} indicates the intramolecular hydrogen bonding is stronger in H$_4$F than in the other ligands, which is also confirmed by the appearance of $\nu(OH)$ and $\nu(NH)$ bands as low as 3149 cm^{-1}. The two bands in the 1624–1605 cm^{-1} region are due to two C=N groups [22]. In the IR spectra of the complexes the bands in the 1674–1655 cm^{-1} region disappear, suggesting the destruction of the C=O group. The duplet structure of the bands due to the $>C=N$ group in the 1624–1605 cm^{-1} region is lost. The $\nu(C=N)$ band registers a downward shift of 4–19 cm^{-1} and is observed at 1620–1605 cm^{-1} in the IR spectra of the complexes. The intensity of the band in this region is very high compared to those in the IR spectra of the free ligands, which appears to be due to its origin in the stretching vibration mode of the conjugate $>C=N-N=C<$ grouping analogous to those of azines, showing the participation of enolic oxygen in coordination.

A weak band around 1674 cm^{-1} is observed in some of the complexes. This band cannot be assigned to the $>C=O$ group but is due either to an uncoordinated C=N group [24] or combination and overtone bands of benzene ring. This confirms that both the nitrogen atoms of the $>C=N-N=C<$ group (as a result

TABLE II. Important Infrared Spectral Bands of Acyldihydrazones and Their Dioxouranium(VI) Complexes

Complex	ν(OH)+ν(NH)	ν(C=O)	ν(C=N)	Amide II + ν(C—O)(phenyl)	ν(NCO)	ν(C—O)	ν(N—N)	ν(U—O)(phenolic)	ν(U—O)(enolic)	ν(U—N)	ν_3	ν_2
H$_4$A	3328s 3278s 3232s 3181s	1674s 1666s	1624s	1572m 1525s		1271s	1033w					
H$_4$B	3423m 3195s	1673s 1666s	1632s 1612s	1572s 1553s		1269s	1035m					
H$_4$C	3423m 3190s	1673s 1666s	1623s	1572s		1270s	1034m					
H$_4$D	3423m 3186s	1673s 1666s	1623s 1609s	1552s		1275s	1036w					
H$_4$E	3423m 3186	1666s	1623s 1612s	1555s		1278s 1261m	1035w					
H$_4$F	3149s	1655s	1618s	1573s 1554s		1279s 1265s	1032w					
(UO$_2$)$_2$(A)·6H$_2$O (1)	3423m		1674w 1605vs	1589s	1541s	1306m	1035w	603w 538m	490w 400w	360w	926s	247s 243s
(UO$_2$)$_2$(B)·6H$_2$O (2)	3423m		1674w 1612s	1573s	1531s	1299m	1035w	596w 506w	476w 425w	347w 311m	912s	246m
(UO$_2$)$_2$(C)·6H$_2$O (3)	2423m		1606vs	1542m	1542m	1304m	1034w	598m 519m	430m 408m	311m	907s	225s
(UO$_2$)$_2$(D)·6H$_2$O (4)	3422m		1606vs	1590sh	1538s	1296s	1034w	596m	472m 416s	315m	899s	258s
(UO$_2$)$_2$(E)·6H$_2$O (5)	3422m		1653w 1605s		1541w	1311w	1037w	602w	438w 393w		891m	239s
(UO$_2$)$_2$(F)·6H$_2$O (6)	3450s 3150s		1622s	1571s		1317w	1032w	562w 458mbr	438br^a 343w	365w	895m	

^{a}Mixed due to ν(M—O)(phenolic) and ν(M—O)(carbonyl).

of enolization of ligands) are not involved in bonding, instead only one nitrogen atom participates in coordination. Substantial evidence is available for this contention [12, 13]. A lower shift of *ca.* 4–19 cm^{-1}, ν(C=N) is observed on complexation because of the difference of bonded species (H$^+$ or UO$_2{}^{2+}$) to the $>$C=N group.

Here it must be emphasized that the IR spectra of the phthalamido complex shows a positive shift in the ν(C=N) stretching frequency as compared to that in the parent ligand. This fact can be correlated as follows. In the phthalamido complex, the electron density from the phenyl ring of salicylaldimine flows to the uranyl ion through the azine group nitrogen atoms, increasing carbon and nitrogen bond order, as has been reported in thiosemicarbazonato complexes [34], while in other complexes the drainage of π-electron density of the phenyl ring towards the uranyl ion upon coordination occurs through the oxygen atom, which is also supported from the low frequency IR spectral region of the complexes. The ν(M–O)(phenolic) in the phthalamido complex occurs at 562 and 458 cm^{-1} as compared to the 606–596 and 538–506 cm^{-1} regions for ν(M–O)-(phenolic) in the remaining complexes. For the same reason ν(M–N) in the phthalamido complex occurs at higher frequency (380, 343 cm^{-1}) as compared to
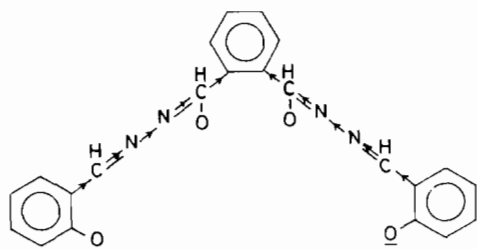
the 347–311 cm^{-1} region for the other complexes. The flow of electron density to the uranyl ion through the azine group can be attributed to the replacement of methylene groups by a phenyl ring, which exerts electron-withdrawing power over the salicylaldiminato phenyl ring in the phthalamido ligand between two hydrazone parts. However, the IR spectrum of the copper(II) phthalamido complex shows a negative shift [33] in ν(C=N) frequency, an usual trend observed in general in acylhydrazone complexes. This fact can be understood readily in terms of higher electronegativity of copper than uranium, which puts a check on the electron-withdrawing power of the phenyl ring.

The ligand band in the 1573–1552 cm^{-1} region arises due to mixed contributions of the amide II and phenyl group. In some ligands, the band due to amide II and ν(C–O) are split. In the IR spectra of the complexes, the bands in the 1573–1552 cm^{-1} region are shifted to higher frequency, indicating the involvement of phenolic C–O group in bonding. The position

of ν(C–O) is diagnostic of binuclear structure through oxo-bridging [25, 26]. In the IR spectra of the complexes, a new weak to medium to strong band in the 1542–1531 cm^{-1} region is observed. This band is characteristic of the enolization of ligands in the complexes and may be assigned to ν(NCO) [29] vibrations. Of some significant interest are the marked spectral changes caused by the formation of the metal complexes in the 1300–1100 cm^{-1} region [28]. Bands appearing in the 1279–1261 cm^{-1} region in the ligand may be assigned to bending vibrations of the phenolic C–O group. The bands in this region show considerable higher frequency shifts in the metal complexes and appear in the 1305–1275 cm^{-1} region, indicating involvement of the phenolic C–O group in chelation. From the above discussion it is evident that ligands coordinate to the uranyl ion in an enol form and act as tetrabasic hexadentate ligands and coordinate through phenolic and enolic oxygen and azomethine nitrogen. The hexadentate nature of the ligands is further confirmed by far IR spectra, where bands are observed around the 606–588, 538–506; 485–430, 425–393 and 380–347, 332–302 cm^{-1} regions, which can be assigned to ν(U–O)-phenolic; ν(U–O)(enolic) and ν(U–N) vibrations, respectively [30].

All the uranyl complexes show strong absorption at the *ca.* 923–891 cm^{-1} region, assigned to the ν_3 vibrations of the uranyl group. The ν_1 vibration of the uranyl group is not observed in the IR spectra of the complexes. The ν_1 mode of the uranyl group is IR forbidden in the free linear ion. The Raman spectrum of complex 3 recorded as a representative sample shows a very strong broad band centred at 860 cm^{-1}. The absence of a band around 860 cm^{-1} in the IR spectra of the complexes and appearance of a strong band in the Raman spectra suggests that the linearity of the UO$_2{}^{2+}$ group is maintained in the complexes. The double degenerate OUO bending mode is observed as a medium to strong band in the 246–239 cm^{-1} region in the low frequency IR spectra of these complexes.

The appearance of only one absorption band due to ν_3 vibration in the complexes indicates that both the uranyl groups are in the same coordination environment [16]. This fact coupled with the presence of oxo-bridged phenolic oxygen suggests that two hydrazone parts of the ligands are attached to different uranyl groups in a symmetric linear fashion leading to polymeric structure, the two uranyl groups attached to different ligand molecules being held together by phenolic oxo-bridges. Alternatively, this suggests that the ligands act as bridge molecules.

In an attempt to study the effect of complexation on the coupling of C=O vibrations, either as such or in an enolized form and of ligand coordination to uranyl ion as a function of the number of methylene

groups, we compared the asymmetric stretching vibrations of the uranyl ion in various complexes recorded under identical conditions. It is interesting to note that ν_3 vibrations decrease in the order $\nu_{3(oxamide)} > \nu_{3(malonamide)} > \nu_{3(succinamide)} > \nu_{3(glutaramide)} > \nu_{3(phthalamide)} > \nu_{3(adipamide)}$. The successive decrease of ν_3 values must be attributed to the decrease of O=U=O bond order due to coordination of enolized carbonyl oxygen atom. In other words, the lowering of ν_3 appears to have taken place by the increasing drainage of π_{2p}-electron density from the oxygen of the $>$C—O group to the uranium atom, which has been facilitated by decreasing coupling between them. This observation enables us to infer that the coupling between two $>$C—O groups of the coordinated ligands decreases with the increase in the number of methylene groups in the ligands whose $>$C—O groups are coordinated to uranium(VI) and lends support to the proposition made by Rivest and Jain [35] from their studies on the oxamido and malonamido complexes. Considering the composition of the complexes, their insolubility in the common organic solvents, high decomposition temperature, the tetrabasic hexadentate nature of the ligand, the presence of oxo and ligand bridging, it can be suggested that all the dioxouranium(VI) complexes possess polymeric structure involving an eight-coordinated uranium atom with six ligand atoms [five oxygen atoms {two (one enol and one phenol) from half of the one enolized ligand molecule, two from water molecules, one from oxo-bridged oxygen atom from the half of the other ligand molecule} and one nitrogen atom of the azine group of the half of the first ligand molecule] forming an equatorial ring in a plane perpendicular to the linear uranyl group (Fig. 2).
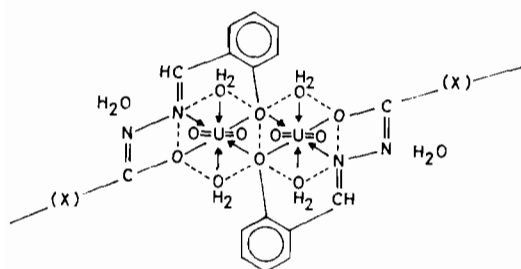

Fig. 2. $(UO_2)_2(L)\cdot 6H_2O$; $H_4L = H_4A$, H_4B, H_4C, H_4D, H_4E and H_4F.

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