Synthesis and spectral studies of sodium acetato and fluorobis-[bis-(o-hydroxynaphthaldehyde)oxaloyldihydrazonato]-tetraaquotetrakisdioxouranate(VI) complexes

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The complexes Na₄[(UO₄)₄(napoxlh)(CH₃COO)₄]·4H₂O (I) and Na₄[(UO₂)₄(napoxlh)]₂F₂·(H₂O)₄ (2) have been synthesized from bis(o-hydroxynaphthaldehyde)oxaloyldihydrazine (napoxlh) and characterized by elemental analysis, molar conductance, electronic, IR and 'H NMR spectroscopic studies. On the basis of these studies, it is suggested that the fluoro complex exists in chair conformation in which coordination of both azomethine nitrogen atoms of the dihydrazine in cis-configuration to the same metal centre leads to coupling between azomethine protons. In acetato complex, the coordination of two hydrazine parts of the dihydrazine even in cis-configuration to different metal centres eliminates the possibility of azomethine proton coupling and thus its existence in chair conformation. All of the complexes involve eight-coordinated uranium atom with the dihydrazine in the enol form.

The interest in the structural, biological and analytical applications of hydrazides and hydrazones has led to a considerable amount of work on their transition metal complexes. Although, simple hydrazide and hydrazone metal complexes have been studied to a considerable extent, those of polyfunctional dihydrazones containing azomethine, amide and phenol functions in duplicate have much less been studied. Bis(o-hydroxynaphthaldehyde)oxaloyldihydrazine is an example of polyfunctional dihydrazine which contains naphthyl fragment and planar oxaloyl-fragment in its molecular skeleton and has the potential to yield complexes having discrete molecularity. In view of the absence of work on such dihydrazones and importance of uranyl complexes in solar energy conversion system, it was of interest to synthesize and characterize dioxouraninium(VI) complexes of the title dihydrazine.

Experimental
All the reagents used were of AR(BDH) or E Merck grade. Oxaloyldihydrazine was prepared by reacting diethyl oxalate (1 mol) with hydrazine hydrate (2 mol). Bis(o-hydroxynaphthaldehyde)oxaloyldihydrazine was prepared by refluxing hot dil. ethanol solution of oxaloyldihydrazine (1 mol) with o-hydroxynaphthaldehyde (2 mol). The yellow precipitate obtained was recrystallized from ethanol, dried in an oven at 70°C, m.p. > 300°C, (dec). Anal: [Found: C, 68.00; H, 4.25; N, 13.32%; Reqd. for C₂₄H₁₈N₄O₄, C, 67.60; H, 4.23; N, 13.15%].

Uranium and sodium in the complexes were determined by standard literature methods. Carbon, hydrogen and nitrogen were determined microanalytically. Fluoride was determined as lead chlorofluoride. Water molecules were determined by heating the sample in an oven at 110°C and 180°C, respectively, and passing the vapour through a trap containing anhydrous copper sulphate which turned blue and the weight loss was estimated. The molar conductance of the complexes at 10⁻³ M dilution in DMSO were measured on Direct Reading Conductivity meter with a dip-type conductivity cell. The IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer in the range 4000-400 cm⁻¹ in KBr discs. The 'H NMR spectra were recorded on a CFT-20, 90 MHz spectrometer in DMSO-d₆ solution using TMS as an internal standard. The electronic spectra of the ligand and complexes in DMSO were recorded on a Milton Roy Spectronic-21 spectrophotometer in the range 300-800 nm.

Preparation of Na₄[(UO₂)₄(napoxlh)(CH₃COO)₄]·4H₂O (1)
To an ethanolic solution of UO₂(CH₃COO)₂·3H₂O (0.05 M, 60 cm³) in ethanol containing a trace of acetic acid, was added a hot solution of dihydrazine (0.02 M, 50 cm³) in ethanol. The solution was refluxed for 2 h which on cooling gave a brown precipitate. This was filtered, washed with hot ethanol, benzene and ether and dried over anhydrous CaCl₂.

The precipitate obtained above was suspended in ethanol (50 cm³) to which CH₃COONa in ethanol was added maintaining UO₂(CH₃COO)₂·3H₂O·CH₃COONa molar ratio as 1:8. This reaction mixture was refluxed for 4-6 h. The reddish brown precipitate was filtered, washed with aq. ethanol, ethanol, benzene, ether and dried over anhydrous CaCl₂.

Yield 85% Anal: [Found: Na, 3.74; U, 40.21; C, 27.59;
Preparation of Na₄[(UO₂)₄(napoxl)₂F₄(H₂O)₄] (2)

This complex was prepared by the above procedure by adding NaF dissolved in minimum amount of water in place of CH₃COONa to the precipitate obtained from reaction of UO₂(CH₃COO)₂·2H₂O with dihydrazone under reflux in 3:1 molar ratio. The reddish brown precipitate obtained was filtered, washed with aq. ethanol, ethanol, benzene and ether, and dried over anhydrous CaCl₂. Yield 90% Anal: [Found: Na, 4.31; U, 43.58; C, 26.98; H, 1.65; N, 5.08; F, 3.53; Req'd. for Na₄U₄C₃₂H₃₆N₆O₂₂F₄: Na, 4.25; U, 43.99; C, 26.62; H, 1.66; N, 5.18; F, 3.54%].

Results and discussion

All the complexes are air stable up to 300°C and decompose above this temperature. The complexes are insoluble in common organic solvents and are soluble in highly coordinating solvents like DMF and DMSO. The complex (1) shows weight loss corresponding to four water molecules at 110°C indicating their presence in the lattice structure of the complex. Both the complexes show weight loss corresponding to four water molecules at 180°C suggesting that they are coordinated to the metal centre. The complexes show molar conductance values of 132.0 and 120.5 ohm cm⁻¹ mol⁻¹ in DMSO suggesting that they are 4:1 electrolytes in this solvent.

The polyfunctional dihydrazone can exist in the complexes either in the staggered configuration (structure 1) or cis-configuration in keto, keto-enol or enol forms. Further, in cis-configuration, the dihydrazone can bind to the metal ion in mode I (structure 2A) or in mode II (structure 2B). The broad signal due to δOH + δNH protons observed at 12.72 ppm in the ¹H NMR spectrum and very strong carbonyl band at 1655 cm⁻¹ in the IR spectrum of the uncoordinated dihydrazone disappears on complexation. The strong broad band in the region 3500-3300 cm⁻¹ and strong bands at 3382, 3332 and 3298 cm⁻¹ assigned to have composite nature due to phenolic –OH and secondary –NH groups are displaced by strong band in the region 3550-3000 cm⁻¹ in the IR spectra of the complexes. Such features associated with ¹H NMR and IR spectra of the complexes confirm collapse of amide structure of the dihydrazone due to its enolization and consequent coordination to the metal centre through phenolate and enolate oxygen atoms. The 6-CH=N signal observed at 89.72 ppm shows a downfield shift by 0.35-0.48 ppm in the ¹H NMR spectra and the νC=N band observed at 1616 cm⁻¹ shifts to lower frequency by 15-20 cm⁻¹ and appears in the region 1601-1594 cm⁻¹ in the IR spectra of the complexes indicating coordination of the dihydrazone to the metal centre through azomethine nitrogen atoms. A very strong νC=N band due to enolization is characteristic of the presence of >C=N–N=C< group in the complexes.

The IR spectrum of the free dihydrazone shows a strong band at 1528 cm⁻¹ which is assigned to amide II + ν(C – O) (phenolic). The complexes show strong to very strong band at 1529 and 1531 cm⁻¹, respectively, assigned to νNCO⁻ vibration of the newly formed NCO⁻ group. The ν(C=O) (phenolic) band appears at 1555 cm⁻¹ in complex (2) and this shows a positive shift of 27 cm⁻¹ as compared to its position at 1528 cm⁻¹ in the free dihydrazone indicating that the phenolic oxygen atom is involved in oxo-bridging in this complex. The new medium intensity band observed at 810 cm⁻¹ in this complex is characteristic of M = M grouping. On the other hand in the complex (1), the νC–O (phenolic) indicates coordination through phenolic oxygen atom and dismisses the possibility of its involvement in oxo-bridging. In this complex, the νas(COO) and νs(COO) appear at 1555 and 1429 cm⁻¹ which are characteristic of bridging bidentately coordinated acetate group. The ν₅(UO₄²⁻) stretching frequency in these complexes appear at 888 and 907 cm⁻¹ as strong bands. The new weak intensity bands are observed at 514 and 446-469 cm⁻¹ which may be assigned to ν(M – O) (phenolic) and ν(M – O) (carbonyl). The complex (2) shows a new weak intensity band at 487
cm⁻¹ which is assigned to ν(U–F) stretching frequency.

It may be noted that δ – CH = N signal in the ¹H NMR spectrum of the complex (2) appears as a quartet as compared to a singlet in the complex (1) and the free ligand. Such a feature of ¹H NMR spectrum of the complex (2) is similar to our earlier observation and is a direct evidence for coupling between azomethine protons. This suggests that the complex exists in chair conformation in which equatorial and axial protons absorb at different field strengths. The chair conformation of the complex arises due to steric crowding in the molecule resulting from coordination of both azomethine nitrogen atoms and both phenolic oxygen atoms of the same dihydrazone molecule to the same metal ion in the cis-configuration (structure 2A). In this conformation, the axial azomethine protons absorb at higher field (09.55, 10.03 ppm) as compared to equatorial azomethine protons which absorb at lower field (10.18, 10.65 ppm). The pattern of the azomethine proton signals is asymmetric in nature. This is the consequence of interchange between the two types of azomethine groups as a result of nitrogen inversion around the uranyl groups. Broadness of the lines may be due to the nitrogen inversion at a sufficiently slow rate at metal centre as compared to that in the complex (1). This may be related to stronger bonding between azomethine nitrogen atom and uranium atom as a result of coordination of highly electronegative fluorine atom to the metal centre which attracts electron density towards itself causing greater flow of electron density from azomethine nitrogen atoms to the uranium atom.

The existence of azomethine protons in the equatorial and axial positions in complex (2) may suggest that one hydrazone part of the dihydrazone would tend to attain axial position while the other hydrazone part remains in the equatorial position. Consequently, groups in the axial position would absorb at lower frequency as compared to their equatorial counterpart. On the other hand, the uranyl ion would tend to arrange the ligand donor atoms around it in a plane perpendicular to it because of its strong tendency to exert strong axial force. The uranyl ion in the present complex exists as linear uranyl group as the IR spectra of the complex shows only one strong band at 888 cm⁻¹ assignable to its ν₅(UO₄²⁻) stretching frequency. Thus the arrangement of ligand donor atoms around the linear uranyl groups is a function of these two opposite factors which consequently lead to quasiplanar arrangement of donor atoms around the uranyl ion.

The absorption spectrum of napoxlhH₄ is characterized by two peaks at 330 and 370 nm in the region 300-400 nm which arise from intraligand π → π* and n → π* transitions. The complexes show bands at 330, 390, 450, 500 nm and 330, 395, 455, 530 nm, respectively. The band at 330 nm remains practically unshifted whereas the band at 370 nm shows a red shift of ~ 20 nm indicating involvement of ligand in coordination. The band at 450 nm is assigned to have its origin due to charge transfer from equatorial donor atoms to the uranyl ion. The band characteristic of uranyl ion appears at 500 nm and 530 nm which arises from transfer of charge from equatorial oxygen atom to uranium atoms.

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References