Synthesis and spectral characterization of dioxouranium(VI) complexes of salicylhydrazine and acetone salicylhydrazone

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Abstract. Dioxouranium(VI) complexes of the types UO_2LSO_4 and $UO_2L_2SO_4$ (where L = SH, ASH) have been prepared from reaction of uranyl sulphate with salicylhydrazine (SH) and acetone salicylhydrazone (ASH) and characterized by conventional chemical and physical measurements. Infrared and Raman spectra indicate that *mono-* and *bis*-complexes contain six- and seven-coordinate uranium atom respectively with all the ligand atoms arranged in an equatorial plane around the linear uranyl group. The infrared spectra (4000–200 cm^{-1}) reveal that both SH and ASH act as neutral bidentate ligands coordinating through a carbonyl oxygen and primary amine/azomethine nitrogen atoms. The sulphato group coordinates to the uranyl ion as bidentate chelating ligand and terminal monodentate ligand in mono- and bis-complexes respectively.

1. Introduction

Acylhydrazines (Zabalpurwala *et al* 1964; Sen Gupta and Dutta 1971, 1975; Alcock *et al* 1972; Iskander *et al* 1974; Biradar and Angadi 1976; Singh *et al* 1984b) and acylhydrazones (Narang and Aggarwal 1975; Aggarwal and Rao 1977, 1978; Pardhy *et al* 1979; Aggarwal *et al* 1981; Dutta and Sarkar 1981; Dutta and Hossain 1982; Johnson *et al* 1982; Patil *et al* 1982, 1983; Dutta and Das 1983; Singh *et al* 1984a; Lal *et al* 1986b) have been known to give stable complexes with transition and non-transition metal ions, yet their uranyl complexes have not been studied in detail (Zabalpurwala *et al* 1964; Aggarwal and Prasad 1971; Biradar and Angadi 1976; Paolucci *et al* 1985). The uranyl ion has strong affinity for oxygen donor ligands because of its hard acceptor properties (Sutton 1949; Cefola *et al* 1962; Pearson 1968; Khanolkar *et al* 1973; Deshpande *et al* 1977) and offers a large number of geometric structures usually hexa- to deca-coordinate (Zachariasen 1954; Wells 1966; Cattalini *et al* 1971; Ahuja and Singh 1973, 1977). In continuation of our recent study on the synthesis and structural assessment of dioxouranium(VI) complexes of aroylhydrazines and aroylhydrazones (Lal 1986; Lal *et al* 1986a), the present paper describes the preparation, characterization and infrared and Raman spectral features of the coordination compounds of the type UO_2LSO_4 and $UO_2L_2SO_4$ formed by the interaction of uranyl sulphate with SH and ASH which have been found to contain 6- and 7-coordinated uranium atom in mono- and bis-complexes respectively.

Chart 1.

Chart 2.
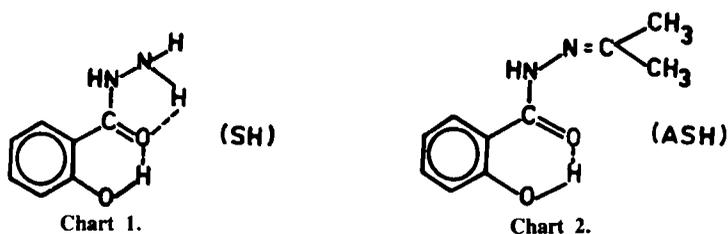
2. Experimental

2.1 *Materials and measurements*

Uranyl sulphate, ethyl salicylate, acetone and hydrazine hydrate used were from BDH, and were AR or equivalent grade. SH, m.p. 147 (lit. 148°C), was prepared by the method of Struve and Radehausen (1984). ASH, m.p. 206 (lit. 205°C), was prepared by condensing acetone with salicylhydrazine and recrystallized from ethanol (Ma and Tien 1953). Uranium in the complexes was estimated as U_3O_8 (Vogel 1973, p. 539). Sulphate was estimated as $BaSO_4$ (Vogel 1973, p. 462). Hydrazine was estimated volumetrically by KIO_3 after submitting the complexes to acid hydrolysis for ~ 4 h (Vogel 1973, p. 380). Nitrogen was analysed by microanalysis. Molecular weight of the complex $UO_2(ASH)SO_4$ was determined as a representative sample by Rast's method using diphenyl as a solvent (Mann and Saunders 1964). The molar conductance of the complexes at 10^{-3} M dilution in DMF was measured using an Elico conductivity bridge model CM-82T with a dip-type conductivity cell. IR spectra of the ligands and their complexes were recorded on Perkin-Elmer 577 spectrophotometer in CsI pellets in $4000-200$ cm^{-1} region. Raman spectra were recorded on a Raman spectrophotometer (Ramalog 1403) in KBr by employing rotating sample technique to avoid decomposition of the sample.

2.2 *Preparation of the complexes*

The complexes were prepared by the following procedures.

(a) *Preparation of* UO_2LSO_4 *(L = SH, ASH) complexes*: The uranyl sulphate (50 ml, 0·01 M) in hot methanol was added into a solution of the ligand (110 ml, 0·01 M) in hot methanol and the mixture heated on a steam bath for about an hour with stirring. The precipitation of the complexes was effected by adding ether to the solution which was then concentrated to 90 ml and cooled to room temperature. The complexes were filtered by suction, washed with methanol and finally with ether and dried over anhydrous calcium chloride in a desiccator and then in an electric oven at 60–70°C.

(b) *Preparation of* $UO_2L_2SO_4$ *(L = SH, ASH) complexes*: The uranyl sulphate (1 g) was suspended in 100 ml hot ethanol. To this suspension, the ligand in ethanol (0·01 M) was added with continuous vigorous stirring maintaining the molar ratio at 1 : 2. The solution was refluxed for two hours and this precipitated the complex. The complex was filtered and washed with ethanol and ether and collected as above.

3. Results and discussion

The complexes isolated in the present study, their analytical data, melting point (decomposition point) and molar conductances are presented in table 1. Partial spectral data for the ligands and their complexes are presented in table 2.

The results of elemental analyses are consistent with 1 : 1 and 1 : 2 metal-to-ligand stoichiometry and accordingly these complexes have the general formula $[UO_2LSO_4]$ and $[UO_2L_2SO_4]$ (where L = SH, ASH). The molecular weight of the complex $UO_2(ASH)SO_4$ determined as a representative sample (found, 538; calcd., 558) is compatible with the above stoichiometry. The complexes are sparingly soluble in ethanol and methanol but completely soluble in DMF only. The conductance measurements in DMF are in accord with the non-electrolytic nature (Geary 1971) of the complexes. Slightly higher values may be due to their partial solvolysis in the highly coordinating solvent DMF (Livingstone and Oluka 1978; Saha and Bhattacharya 1982).

Contributions due to the coordinated ligands were selected by comparing the IR spectra of the complexes with those of the free ligands and the residual features were assigned to the coordinated sulphato groups. Strong bands due to sulphato group are believed to superimpose and mask some of the ligand bands. SH shows absorption bands at 3333s, 3283s, 3151m while ASH shows a strong band at 3283 cm^{-1} and a strong broad band in the 3200–3000 cm^{-1} region (Mashima 1962). These bands are assigned to νNH and νOH vibrations. The medium to strong band present in the 2800–2700 cm^{-1} region of the IR spectra indicates the presence of strong intramolecular hydrogen bonding in the ligands.

The $UO_2(SH)SO_4$ complex shows a strong broad band in the 3600–3400 cm^{-1} region and another strong broad band in the 3353–3000 cm^{-1} region with maximum absorption at 3290 cm^{-1} while the $UO_2(SH)_2SO_4$ shows one strong broad band in the 3600–3400 cm^{-1} region and another very strong broad band in the 3350–2900 cm^{-1} region. The $UO_2(ASH)SO_4$ complex shows a single medium broad band in the 3600–3100 cm^{-1} region with maximum absorption at 3475 cm^{-1} while the $UO_2(ASH)SO_4$ complex shows a medium broad band in the 3600–3394 cm^{-1} and a very strong broad band in the 3354–3000 cm^{-1} region. The presence of only one band in the IR spectrum of $UO_2(ASH)SO_4$ with maximum absorption at 3475 cm^{-1} suggests that the secondary amine group does not participate in bonding and $-OH$ group freed from intramolecular hydrogen bonding absorbs at higher frequency. The essentially different character of absorption bands in the 3600–2900 cm^{-1} region of IR spectra of $UO_2L_2SO_4$ (where L = SH and ASH) complexes compared to those of UO_2LSO_4 (where L = SH, ASH) complexes may be attributed to the development of a new intramolecular hydrogen bonding between OH groups of the salicyl grouping of the two ligands coordinated to the uranyl ion.

The most outstanding feature of the IR spectra of the uranyl complexes studied here is observable in the 1700–1500 cm^{-1} region which contains bands due to $>C=O$, $>C=N$, $-NH_2$ and C–O group frequencies. In the complexes, amide I band appearing at 1645 cm^{-1} and 1650 cm^{-1} and δNH_2 and $\nu C=N$ appearing at 1630 and 1620 cm^{-1} in uncoordinated SH and ASH respectively suffer marked negative shift and appear in the 1635–1630 and 1618–1600 cm^{-1} region respectively. The lowering of $\nu C=O$ and $\nu C=N/\delta NH_2$ bands is attributed to the drainage of

electron density from oxygen of $>C=O$ group and nitrogen of $>C=N$ or NH_2 group as a result of oxygen-to-metal and nitrogen-to-metal coordination (Zabalpurwala et al 1964; Paul and Chadha 1969; Sen Gupta and Dutta 1971, 1975; Alcock et al 1972; Iskandar et al 1974; Narang and Aggarwal 1975; Biradar and Angadi 1976; Aggarwal and Rao 1977, 1978; Pardhy et al 1979; Aggarwal et al 1981; Dutta and Sarkar 1981; Dutta and Hossain 1982; Johnson et al 1982; Patil et al 1982, 1983; Dutta and Das 1983; Singh et al 1984a,b; Woon et al 1985; Lal et al 1986b). The lowering in amide I, $\nu C=N$ and δNH_2 vibrations is of the magnitude expected for complexes in which the $>C=O$, $>C=N$, $-NH_2$ groups and negatively charged ligands (SO_4^{--}) constitute the first coordination sphere around the uranyl group. The involvement of $>C=O$ group in coordination is also confirmed from the fact that the amide II band at 1585 cm^{-1} in SH and 1595 cm^{-1} in ASH also suffers a considerable negative shift and appears in the 1560–1550 cm^{-1} region as either medium band or strong band in the IR spectra of the complexes. The IR spectra of the uncoordinated SH and ASH show absorption band at 1525 cm^{-1} which is assigned to C–O (phenolic) stretching (Rastogi et al 1978). This band remains unaltered in position and intensity in the IR spectra of the complexes. Such a feature of this band clearly indicates the absence of interaction between $-OH$ of salicyl group and uranyl ion (Issa et al 1967).

In addition to the ligands and sulphato group bands, the rock salt region IR spectra of the uranyl complexes studied here show very strong broad absorption bands in the 922–915 cm^{-1} region. This band is assigned to asymmetric stretching vibration ν_3 of uranyl group. Complexes 1 and 3 show weak absorption bands at 842 and 850 cm^{-1}. The symmetric stretching vibration ν_1 is IR-forbidden. However, the forbidden vibrations may become allowed as a result of particular symmetry properties of the molecules. The absence of a strong band assignable to ν_1 implies that the linearity of the UO_2^{2+} group is maintained in these complexes. The Raman spectra of $UO_2(SH)SO_4$ and $UO_2(ASH)SO_4$ complexes were recorded as representative samples in the 900–800 cm^{-1} range and show a strong broad band centred at 855 and 852 cm^{-1}. The OUO bending vibration occurs as a medium to strong band in the 260–255 cm^{-1} region in the low frequency IR spectra of these complexes. The OUO bending mode in ASH complexes masks a weak ligand band at 255 cm^{-1}.

The UO_2LSO_4 (L = SH and ASH) complexes show four bands at 1245, 1190, 1155, 1100 and 1225, 1190, 1175, 1155 cm^{-1} respectively masking ligand bands in the 1250–1100 cm^{-1} region. The strong broad band due to triply degenerate ν_3 mode in the ionic sulphate splits into three bands when sulphato group coordinates to the metal ions as a bidentate chelating ligand. Although most of the ligand absorption bands in the region 1250–1100 cm^{-1} are masked by strong absorption bands due to sulphato group, one absorption band due to ligand appears as strong as sulphato group absorption band in the IR spectra of these complexes and hence maintains its identity in the spectra. In view of the absence of isotopic substitution studies, it is difficult to assign unambiguously the absorption bands due to sulphato group and ligands definitely. The triply degenerate OSO bending mode ν_4 which occurs as a sharp well-defined band at 610 cm^{-1} in sulphates with T_d symmetry also splits up into its components at 660, 640, 590 cm^{-1} in the complex $UO_2(SH)SO_4$ and 650, 600, 585 cm^{-1} in the complex $UO_2(ASH)SO_4$ respectively. Moreover, the ν_1 band (IR-forbidden in the uncoordinated sulphato) appears at 1030 cm^{-1} as

either a strong or a very strong band. Besides ν_1, ν_3 and ν_4, the ν_2 mode is observed as either a strong or medium intensity band at 480 or 470 cm^{-1} in the low-frequency IR spectral region. The positions of the absorption bands due to sulphato group are consistent with those normally associated with chelating sulphato group (Nakamoto *et al* 1959; Barraclough and Tobe 1961; Baldwin 1963; Cotton and Wilkinson 1972).

The spectra of the $UO_2L_2SO_4$ (L = SH or ASH)-type complexes are essentially different from those of UO_2LSO_4 (L = SH, ASH)-type complexes. In these complexes, the ν_1 and ν_2 appear as either a medium or strong band at 1030 and 1025, and 470 and 480 cm^{-1} respectively. The type of coordination of sulphato group is usually judged from the splitting of ν_3 and ν_4 into its components. In the present complexes, ν_3 mode is split into two strong broad bands (1225–1150 cm^{-1} and 1120–1080 cm^{-1} in complex $UO_2(SH)_2SO_4$ and 1240–1170 cm^{-1} and 1140–1060 cm^{-1} in complex $UO_2(ASH)_2SO_4$. Such a feature of the IR spectra of 1 : 2 complexes is characteristic of sulphato group in C_{3v} symmetry and suggests its monodentate coordination (Nakamoto 1978). The monodentate coordination of the sulphato group is also confirmed from the fact that the sharp well-defined band at 610 cm^{-1} due to triply degenerate ν_4 mode in ionic sulphate splits into a doublet at 630, 600 cm^{-1} in $UO_2(SH)_2SO_4$ and at 640, 605 cm^{-1} in $UO_2(ASH)_2SO_4$ complexes respectively.

Considering that SH and ASH act as bidentate chelating ligands and sulphato group as a bidentate chelating ligand in UO_2LSO_4 (L = SH, ASH)-type complexes and as a terminal monodentate ligand in $UO_2L_2SO_4$ (L = SH, ASH) complexes respectively, the complexes are tentatively assigned monomeric structures (charts 3 and 4) involving six- and seven-coordinated uranium atom in UO_2LSO_4 and $UO_2L_2SO_4$ complexes respectively with four and five ligand atoms arranged around the linear uranyl group.
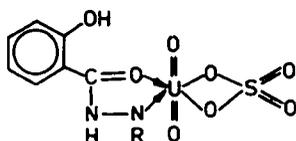

Chart 3

UO_2LSO_4 ; L = SH, ASH;
R = H$_2$(SH), = C(CH$_3$)$_2$(ASH)
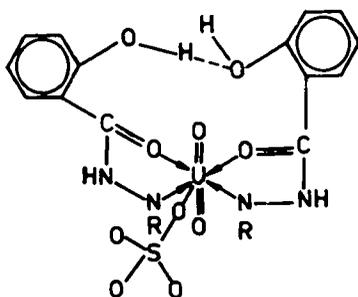
Chart 4

$UO_2L_2SO_4$; L = SH, ASH;
R = H$_2$(SH), = C(CH$_3$)$_2$(ASH)

Acknowledgements

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