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Dioxouranium(VI) complexes with 4-substituted -1-(2-furoyl) thiosemicarbazides.

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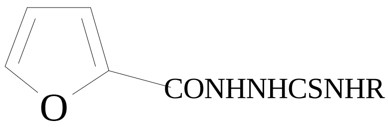
Introduction:

Many of the S and N donor ligands exhibiting carcinostatic and antiviral activities possess the thiosemicarbazide skeleton[1]. Thiosemicarbazide derivatives have been reported to possess antifungal[2], antibacterial[3], herbicidal[4], hypoglycemic[5] and anticonversal[6] activities. Nishie et.al[7] have reported an excellent relationship between the activity and structure. Ability of the thiosemicarbazide to form stable coloured complexes with transition metal ions had led to their photometric determination. The potentiality of S and N donor ligands have attracted the attention of many chemists. Thiosemicarbazides usually act as chelating ligands coordinating through thioketosuphur and nitrogen of hydrazine residue and act as bidentate but in some cases, they behave as monodentate coordinating through only S atom[8]. Thiosemicarbazides are known to form many complexes with transition and non-transition metal ions.

In the present investigation, 4-substituted-1-(2-furoyl) thiosemicarbazides are used as chelating agents for UO_2(II) metal ion. Attempts are made to locate the metal ligand bonding sites and to establish the structure of these complexes from conductance and spectral measurements.

Uranium is known to exhibit a wide range of coordination numbers[9]. The object of the present investigation is to synthesise dioxouranium(VI) complexes with the following ligands.



R = C_6H_5 (PTSC);, C_6H_4Cl (p) (p-ClPTSC);, C_6H_4Br (p) (p-BrPTSC);, $C_6H_4CH_3$ (p) (p-MePTSC);, $C_6H_4OCH_3$ (p) (p-MeOPTSC);, and CH_2—CH=CH_2 (ATSC).

The analytical data shown in Table-1 indicate that the compelxes have 1:1 stiochiometry of the type UO_2LCl_2. All the complexes are stable towards atomosphere and insoluble in common organic solvents.

Molar conductance:

The molar conductance values of the complexes in DMF (10^{-3}M) are given in Table-1. The osbserved molar conductance values lie in the range 12-18 mhos.cm^2.mole^{-1}. The appreciable value of molar conductance in a few cases may be due to partial solvolysis of the complexes in DMF or it may be due to the replacement of NO_3 or Cl in coordination sphere by DMF[10,11] and make the complexes show electrolytic behaviour. In view of these observations, these complexes of dioxouranium (VI) may be regarded as non-electrolytes.

Table-1: Elemental analysis and molar conductance data.

Complex	Analysis % found (Calculated)				Molar conductance Scm^2mol^{-1}.
	M	N	S	Cl	
$UO_2(PTSC)Cl_2$	39.6 (39.4)	6.6 (6.98)	4.92 (5.32)	11.7 (11.79)	12.50
UO_2(p-ClPTSC)Cl_2	37.2 (37.4)	6.8 (6.6)	4.92 (5.04)	11.05 (11.15)	14.20
UO_2(p-BrPTSC)Cl_2	34.65 (34.9)	5.96 (6.2)	4.53 (4.7)	10.26 (10.43)	15.4
UO_2(p-MePTSC)Cl_2	38.44 (38.6)	6.7 (6.8)	5.1 (5.2)	11.4 (11.5)	16.85
UO_2(p-MeOPTSC)Cl_2	37.5 (37.7)	6.3 (6.7)	5.2 (5.1)	11.4 (11.2)	17.95
$UO_2(ATSC)Cl_2$	41.9 (42.1)	7.3 (7.4)	5.4 (5.7)	12.5 (12.6)	16.2

Infrared spectra:

In the current investigation, the IR assignments for most of the major peaks are based on the corresponding assignments made by other workers [12-13] for thiosemicarbazides, thiocarbhydrazides and thiocarbazide derivatives and complexes derived from them.

Two bands observed in the region 3250-3100 cm^{-1} have been assigned to inter molecular hydrogen bonded N—H stretches in the case of the ligands under present investigation. The N—N stretching frequencies have been reported to occur in the region 1010-900 cm^{-1} in various hydrazine derivatives[14-15]. Therefore the bands observed in the region 1020-970 cm^{-1}

have been assigned to N—N stretch in free ligands. These bands remain unaltered or undergo slight positive shift in complexes indicating non participation of NH in coordination with metal ions.

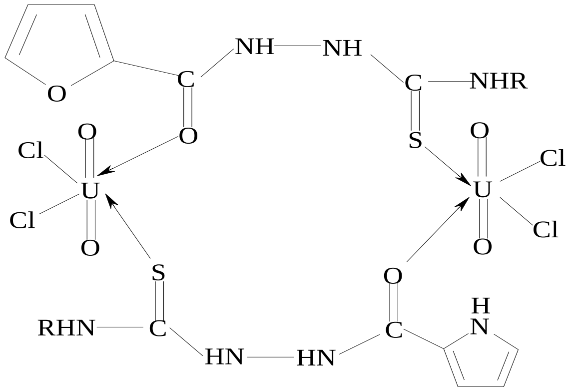
Medium and strong intensity bands in the region 1650-1610 cm^{-1} have been assigned to C=O stretching vibrations. These bands become very weak in intensity or undergo red shift of 30-60 cm^{-1} indicating coordination through C=O oxygen atom to the metal ion.

The bands due to SH and OH around 2600 cm^{-1} and 3400 cm^{-1} have not been observed indicating that the ligands remain in thione and keto form in the solid state. The band due to C-O-C stretch (furan ring) is observed in the region 1290-1250 cm^{-1} is unaltered in the complexes indicating the non participation of furan oxygen atom in complexation.

The ligand bands observed in the regions 1560-1500 cm^{-1}, 1390-1300 cm^{-1}, 1085-1025 cm^{-1} and 780-730 cm^{-1} are assigned to thioamide bands I, II III and IV respectively. On complexation, the tioamide band I shows slight red shift and thioamide II and III bands show lower frequency shift of 5-10 cm^{-1} with intensity variation. Thioamide IV band which is mainly due to C=S stretch suffers a negative shift of 10-30 cm^{-1} with reduced intensity in all the complexes indicating the coordination through thioketo sulphur.

A weak to medium intensity non ligand bands in the region 460-410 cm^{-1} have been assigned to M—O stretch, the peaks in the region 320-290 cm^{-1} and 280-260 cm^{-1} have been assigned to M—S and M—Cl stretches respectively.

Based on the above discussion, the following structure is proposed for the complex.



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