

Fig. 1. Specific conductance-concentration curve of the compounds in chlorosulphuric acid at 35°C. ○, potassium chloride; △, acetic anhydride; ▲, benzoic anhydride; ●, succinic anhydride; ×, phthalic anhydride; ●, 3-nitrophthalic anhydride; ◇, maleic anhydride.

the solute. This is consistent with the following mode of ionization.

$$(RCO)_{2}O + 2HSO_{3}CI = RCO^{+} + RCO_{2}H_{2}^{+} + 2SO_{3}CI^{-}$$
(1)

$$(\text{RCO})_2\text{O} + 4\text{HSO}_3\text{C} \models 2\text{RCO}_2\text{H}_2^+ + \text{S}_2\text{O}_3\text{C}\text{I}_2^- + 2\text{SO}_3\text{C}\text{I}^- \qquad (2)$$
$$\textbf{R} = \text{C}\text{H}_3 \text{ or } \text{C}_3\text{H}_4.$$

$$= CH_3 \text{ or } C_6H_5.$$

The NMR spectra of their solutions in HSO₃Cl contained only 1 peak shifted to lower field. This is assigned to the methyl or phenyl protons of the acidium (RCO₂H₂⁺) ion. This assignment is reasonable, as the peak due to these protons has been observed at about the same position in solutions of acetic and benzoic acids in SbF₃-HSO₃F, where formation of the acidium ion has also been proposed [7]. The C = OH⁺ proton peak could not be observed, presumably due to exchange with the solvent proton[6, 7]. Ionization according to eqn (1) is ruled out by the absence of any band attributable to the C=O⁺ stretching vibration in the region 2200-2300 cm⁻¹ observed in solutions of acetic acid, acetyl halides and benzoyl chloride in H₂S₂O₇[8, 9] where the existence of the acyl ion has been proposed. A broad band was, however, observed at around 1600 cm⁻¹ (Table 3) and is attributed to the C=O stretching vibration of the acidium ion. It has been shown that the C=O

Notes

stretching vibrations characteristic of the acidium ion[10] occur at about 1600 and 1550 cm⁻¹. The lower frequency band could not be observed owing to a strong polyethylene absorption in this region.

The dicarboxylic acid anhydrides behave as weak bases with $\gamma < 1.00$ (Table 1). The average value of the dissociation constant (K_b) of the corresponding conjugate acid is shown in Table 1.

The NMR spectra of the above mentioned compounds in HSO₃Cl contained only 1 sharp peak at a slightly lower field ($\Delta \approx 0.50$ ppm) compared with its position in CDCl₃. In the IR spectra of these compounds in HSO₃Cl, there was no band either in the 2200-2300 cm⁻¹ region characteristic of C=O⁺ or at around 1600 cm⁻¹ characteristic of the acidium ion (C=OH⁺). Hence ionization involving ring-opening is ruled out and simple protonation at ethereal or carbonyl oxygens may occur.

The C-O-C stretching vibrations band was unfortunately obscured by a broad acid band and thus the only way to fix the site of protonation was to examine the change in the C=O stretching frequency. The observed marked shift to lower wave numbers (Table 3) suggests protonation at the C=O group. The appearance of a single strong broad band for C=O group rules out any suggestion involving protonation exclusively on one C=O group which would give two different C=O frequencies. It is concluded that proton exchange between the carbonyl oxygens makes them equivalent.

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Dioxouranium(VI) complexes with ligands containing ONO sequences

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THE HYDRAZONES are capable of exhibiting *keto enol* tautomerism. It has been the interest of the authors to know in which of the forms the hydrazones exist, when complexed with the transition metals. There are examples in the literature where the hydrazones can exist in the *keto form* as well as *enol form* [1].

The earlier literature reveals that there is not much information on the complexes of dioxouranium(VI) with hydrazones except a few spectrophotometric studies[2, 3]. This information has given an impetus to synthesize the dioxouranium complexes with hydrazones.

In this paper we wish to report the synthesis and spectral properties of a few uranium(VI) complexes with aroylhydrazones shown below.



EXPERIMENTAL

Materials and methods

Uranyl acetate dihydrate, ethyl benzoate and hydrazine hydrate used for preparing hydrazide, were of reagent grade. Benzoylhydrazide was prepared according to the known method[4]. The substituted aldehydes and acetophenones were prepared according to the standard [5] methods. Hydrazones were prepared by the reaction of benzoylhydrazide (0.01 M) with corresponding aldehyde (0.01 M) in ethanol.

Preparation of the complexes

To an ethenolic solution containing equimolar quantities of hydrazide and aldehyde or acetophenone (0.02 M each), was added a hot ethanolic solution of 0.01 M of uranyl acetate. The reaction mixture was heated for a while on a water bath. The deep red coloured solution deposited micro-crystalline complex after cooling. The complex thus separated was filtered, washed free from the ligand with ethanol and dried in vacuo over fused calcium chloride.

Elemental analysis

Uranium in the complexes was estimated gravimetrically as U₃O₈. The carbon, hydrogen and nitrogen were analysed by micro analytical methods. The results of the elemental analysis are given in Table 1.

Physical measurements

The conductance measurements were carried out on ELICO CM-82 conductivity bridge with a cell having cell constant 0.829 cm⁻¹. The IR spectra of the ligands and the complexes in Nuiol mull were recorded on Beckman IR-20 spectrophotometer in the region 4000-650 cm^{-1} .

RESULTS AND DISCUSSION

The complexes are reddish brown microcrystalline substances insoluble in common organic solvents. They are however, soluble in DMF and DMSO. This insolubility did not permit the molecular weight determination. The results in Table 1 suggest that these complexes have 1:2 stoichiometry.

Conductance

The molar conductance in DMF at the concentration 10⁻³ M fall in the range of 0-1 ohm⁻¹ cm²/mole. These values are too low to account for any dissociation of these complexes in DMF. Hence these can be looked upon as non electrolytes.

IR spectra

All the ligands exhibit a medium intensity broad band in the region 3275-3200 cm⁻¹ and another a weak broad band around 2700 cm⁻¹. These are considered to be associated with the

secondary -NH stretching and hydrogen bonded -OH stretching vibrations, in view of the previous assignments [6, 7].

In the region $1675-1600 \text{ cm}^{-1}$, we observe two bands. Of these two the high frequency band appearing in the region 1675-1650 cm⁻¹ is assigned to the ν (C=O) and other in the region 1625–1610 cm⁻¹ to the ν (C=N) stretch. These assignments closely agree with those made in case of acetophenones[1] and Schiff bases [8].

In the complexes we observe the following.

i. The -NH stretching vibration has been retained in the complexes and appears in the region 3280-3200 cm⁻¹

ii. The C=O and C=N stretching vibrations appear in the low frequency region around 1630 cm⁻¹ and in the region 1615-1590 cm⁻¹ respectively. This is due to the coordination of C=O and C=N groups to the metal ion through oxygen and nitrogen respectively, which decreases the bond orders of carbon to oxygen and carbon to nitrogen links.

iii. The band around 2700 cm⁻¹ is not observed in the complexes and the phenolic C-O in the region 1290-1275 cm⁻⁻ appears in the region 1310-1300 cm⁻¹. This suggests that the o-hydroxy group of the ligands has involved in the bond formation.

Three characteristic frequencies, (viz. $v_1 = 860 \text{ cm}^{-1}$, $v_3 =$ 930 cm⁻¹ and $\nu_2 = 210$ cm⁻¹) can be predicted [9] for UO₂ ion if it is not linear and ν_2 ν_3 are expected to be IR active if it is linear. In the spectra of the complexes we observe a high intensity band in the region 910-895 cm⁻¹ and is attributed to v_3 vibration. This is in close agreement with the previous observations [10]. The low frequency shift of the ν_3 band may be attributed to the strong perturbations in the chelate rings formed in these complexes. Analogous observations have also been reported by Patel et al.[11].



Lig. No. Comple No.	Complex	Emperical formula	% U				% C		% H	
	No.		Found	Calcd.	Found	Calcđ.	Found	Calcd.	Found	Calcd
I	XI	^{U0} 2 ^{(C} 14 ^H 11 ^O 2 ^N 2 ⁾ 2	31,09	31.82	7.38	7.49	44.98	44.91	2.91	2,98
II	XII	^{UO} 2 ^{(C} 15 ^H 13 ^N 2 ^O 2)2	31.00	30.67	7,28	7.22				
III	XIII	U0 ₂ (C ₁₅ H ₁₃ N ₂ O ₂) ₂	30,50	30.67	7.31	7.22				
IV	XIV	^{U0} 2 ^{(C} 15 ^H 13 ^N 2 ^O 2 ⁾ 2	30,00	30.67	7.18	7.22	46.72	46.32	3.78	3.35
v	xv	U02(C14H10N202C1)2	28.73	29.14	6.92	6.86	40.46	41.12	2.62	2.45
VI	XVI	^{U0} 2 ^{(C} 18 ^H 13 ^N 2 ^O 2)2	28.53	28.07	6,55	6,60	49.65	50.94	3.56	3.06
VII	XVII	^{UO} 2 ^{(C} 15 ^H 13 ^N 2 ^O 3)2	29.60	29.39	6.88	6.91				
VIII	XVIII	^{UO} 2 ^{(C} 15 ^H 13 ^N 2 ^O 2 ⁾ 2	30.41	30.67	7.25	7.22				
IX	IXX	$u_{2}(c_{16}H_{15}N_{2}O_{2})_{2}$	29.70	29.60	6.89	6.96	47.86	47.76	3.21	3.16
x	xx	U02(C15H12N2O2C1)2	28,40	28.17	6.65	6.61	42.38	42.27	2.66	2.82

Table 1. Elemental analysis of dioxouranium(VI) complexes with ligands containing ONO sequences

The spectral evidences, analytical data and the conductance measurements suggest that uranium exhibits coordination number 8 in these complexes and seems plausible in view of the known 8 coordinate complexes[12].

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Vibrational spectra of oxidic stannates in relation to order-disorder phenomena

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IN THE course of our investigations concerning the luminescent properties of titanium-activated stannates and zirconates we needed information about the degree of order in our samples. In many cases X-ray analysis alone is not sufficient for the study of order-disorder phenomena; additional information may be obtained from Raman and IR spectra. The Raman and IR spectra yielded some interesting results which are presented in this paper. We will try to give an approximate assignment of the vibrational spectra of the various compounds investigated.

EXPERIMENTAL

All samples except La₂MgSnO₆ and Y₂Zr₂O₇ were prepared from high-purity starting materials by usual ceramic techniques. The preparation of La₂MgSnO₆ has been described elsewhere[1]. Y₂Zr₂O₇ was prepared by heating a 2:1 mixture of Y₂[ZrO(C₂O₄)₂]₃ and Y₂(C₂O₄)₃ for 2 hr at 1200°C. (Compare the preparation of CaZrO₃ in Ref. [2]). All samples were checked by X-ray analysis. IR spectra were recorded on a Hitachi EPI-G3 grating spectrometer (down to 400 cm⁻¹, KBr-pellets) and a Grubb Parsons DM4 spectrometer with a CsI prism (down to 200 cm⁻¹, CsI-pellets). Raman spectra were recorded on a Spectra Physics 700 Raman Spectrometer using an argon ion laser (courtesy Dr. J. H. van der Maas and Mr. T. Visser of this university). All spectra were recorded at room temperature.

RESULTS

The following compounds have been investigated:

a. La₂MgSnO₆ with ordered perovskite structure. In this compound the SnO₆ octahedra do not share oxygen ions and are separated by Mg²⁺ ions. The SnO₆ octahedra are distorted, probably the *O*-orthorhombic distortion like GdFeO₃. In this case the site symmetry of Sn is C_s .

b. Mg_2SnO_4 with spinel structure. The cation distribution is $Mg^{2+}[Mg^{2+}Sn^{4+}]O_4$ (uverse spinel). In the analogous titanium compound the Mg^{2+} and Ti^{4+} ions are ordered on the octahedral sites like in $Zn[LiNb]O_4$. Until now, however, no ordered stannates are known. In the spinel structure each octahedron shares edges with 6 other octahedra. The site symmetry is D_{2d} (disordered) or C_2 (ordered).

c. Sr_2SnO_4 with K_2NiF_4 structure. In this structure each stannate octahedron shares corners with 4 other octahedra so that layers of coupled SnO_6 -octahedra are formed. The site symmetry of Sn is D_{4n} .

d. La_2SnO_7 , $Y_2Sn_2O_7$ and $Y_2Zr_2O_7$. These compounds have an oxygen-deficient fluorite structure. The oxygen deficiencies can be

statistically distributed (fluorite structure, site symmetry of Sn is O_h), or ordered (pyrochlore structure, site symmetry of Sn is D_{3h}). In the pyrochlore structure the SnO₆ octahedra are distorted and share corners.

The following Raman line and IR bands have been observed (s: strong, m: medium, w: weak, sh: shoulder, br: broad; all values are given in cm^{-1}).

La₂MgSnO ₆	R: 675 (s), 610 (w), 584 (w), 490 (m), 462 (w), 427 (s), 383 (m), 361 (m), 337 (s), 312 (sh), 280 (s), 268 (m), 245 (m) IR: 590 (s), 500 (sh), 415 (s), 350 (w), 337 (m), 330 (w)
Mg ₂ SnO ₄	R: 680 (s), 540 (m), 500 (w), 400 (w)
	IR: 665 (sh), 600 (s), 580 (sh), 450 (s), 410 (m)
Sr ₂ SnO ₄	R: 487 (s), 265 (w)
-	IR: 710 (s), 685 (sh), 580 (s), 320 (s)
$La_2Sn_2O_7$	R: 711 (w), 648 (w), 535 (m), 502 (s), 410 (s), 340 (sh) 310 (s) (see Fig. 1)
	IR: 625 (sh), 590 (s), 435 (sh), 405 (sh), 380 (s), 330 (w)
Y ₂ Sn ₂ O ₇	R: 766 (w), 514 (s), 420 (s), 355 (sh), 315 (s)
	IR: 670 (sh), 640 (s), 450 (m), 425 (sh), 390 (s)
$Y_2Zr_2O_7$	R: no lines
	IR: 500 (br).



Fig. 1. Raman spectrum of La₂Sn₂O₇.