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INFRARED AND THERMAL BEHAVIOUR OF THORIUM(IV) AND OXOZIRCONIUM(IV) COMPLEXES OF DIBENZYL SULPHOXIDE

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ABSTRACT

A series of complexes of thorium(IV) and oxozirconium(IV) with dibenzyl sulphoxide having the general compositions $ThX_4 \cdot 2BzSO$ ($X = Cl$, Br, NCS or NO_3), $ThI_4 \cdot 4BzSO$, $Th(ClO_4)_4 \cdot 6BzSO$, $ZrOX_2 \cdot 2BzSO$ ($X = Cl$, Br, I, NCS, NCSe or BPh_4) and $ZrO(ClO_4)_2 \cdot 6BzSO$ were synthesised and characterized by elemental analyses, electrolytic conductivity, moleculer weight, IR, and magnetic susceptibility measurements. TG and DTA of the complexes were also studied.

INTRODUCTION

Considerable attention has recently been focused on the coordination behaviour of sulphoxides [1–3]. Comparatively little is known about sulphoxide complexes of thorium [4–17] and oxozirconium [11,18–21] and their thermal studies. In the present paper some details of the IR, TG and DTA data of dibenzyl sulphoxide (BzSO) complexes of thorium(IV) and oxozirconium(IV) are given. There seem to be no former reports on these complexes in the literature.

EXPERIMENTAL

All chemicals used were of analytical grade. Various thorium(IV) [12] and oxozirconium(IV) [22] salts were synthesised using methods reported earlier. The ligand BzSO was obtained from Merck and used as received.

Preparation of the complexes

All the complexes were obtained by the following general method. The metal salt was dissolved in absolute ethanol and a dehydrating agent (2,2′-dimethoxy propane) and the reaction mixture was warmed on a water

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TABLE 1

Analytical, conductivity and molecular weight data for thorium(IV) and oxozirconium(IV) complexes of dibenzyl sulphoxide

Compound	Metal (%)		S (%)		Anion		Λ_m ($ohm^{-1} cm^2 mol^{-1}$)	Electrolytic nature	Average MW in $PhNO_2$	Formula weight
	Found	Calc.	Found	Calc.	Found	Calc.				
$ThCl_4 \cdot 2BzSO$	27.56	27.81	7.82	7.67	16.81	17.02	5.9	Non-electrolyte	830	834
$ThBr_4 \cdot 2BzSO$	22.69	22.92	6.41	6.32	31.42	31.62	6.3	Non-electrolyte	1003	1012
$ThI_4 \cdot 4BzSO$	13.54	13.97	7.90	7.71	30.01	30.60	57.8	1:2	550	1660
$Th(NCS)_4 \cdot 2BzSO$	24.91	25.10	20.92	20.77	24.62	25.10	4.9	Non-electrolyte	918	924
$Th(NO_3)_4 \cdot 2BzSO$	24.48	24.68	6.92	6.80	–	–	4.2	Non-electrolyte	934	940
$Th(ClO_4)_4 \cdot 6BzSO$	11.21	11.54	9.62	9.55	19.62	19.80	97.5	1:4	396	2010
$ZrOCl_2 \cdot 2BzSO$	14.06	14.26	10.12	10.03	11.42	11.12	4.3	Non-electrolyte	634	638
$ZrOBr_2 \cdot 2BzSO$	12.39	12.51	8.92	8.80	21.82	22.00	5.1	Non-electrolyte	721	727
$ZrOI_2 \cdot 2BzSO$	11.12	11.08	7.84	7.79	30.19	30.93	6.9	Non-electrolyte	815	821
$ZrO(NO_3)_2 \cdot 2BzSO$	13.27	13.16	9.32	9.26	–	–	4.9	Non-electrolyte	682	691
$ZrO(ClO_4)_2 \cdot 6BzSO$	5.42	5.39	11.46	11.38	11.69	11.80	54.9	1:2	557	1686
$ZrO(NCS)_2 \cdot 2BzSO$	13.39	13.32	18.92	18.74	16.72	16.98	6.1	Non-electrolyte	679	683
$ZrO(NCS)_2 \cdot 2BzSO$	11.83	11.71	8.41	8.23	–	–	6.7	Non-electrolyte	767	777
$ZrO(BPh_4)_2 \cdot 2BzSO$	8.91	8.82	6.40	6.20	–	–	5.4	Non-electrolyte	1021	1031

bath with constant stirring. The ligand was added to this metal salt solution in stoichiometric ratio and the resulting mixture was refluxed for 2–3 h. The excess solvent was distilled off and the resulting viscous mass was treated with excess petroleum ether (60–80°C) to precipitate the desired complex. The product was washed and dried in vacuo.

The analyses and other physical measurements were performed as reported earlier [12,22].

RESULTS AND DISCUSSION

Physical and analytical data for the complexes are contained in Table 1. The complexes are anhydrous as is evident from the analytical, infrared and thermal data. The analytical data show that the complexes are well-defined compounds of the general formulae $ThX_4 \cdot 2BzSO$ ($X = Cl$, Br, NCS or NO_3), $ThI_4 \cdot 4BzSO$, $Th(ClO_4)_4 \cdot 6BzSO$, $ZrOX_2 \cdot 2BzSO$ ($X = Cl$, Br, I, NCS, NCSe, NO_3 or BPh_4) and $ZrO(ClO_4)_2 \cdot 6BzSO$.

The conductivity data of the thorium(IV) complexes show that except the iodo and perchlorato complexes all other complexes are non-electrolytes, while the iodo and perchlorato complexes behave as 1 : 2 and 1 : 4 electrolytes, respectively. The oxozirconium(IV) complexes, except the perchlorato complex, are all non-electrolytes. The perchlorato complex dissociates in $PhNO_2$ and behaves uni-bivalently. Data on the molecular weights of the complexes in $PhNO_2$ are given in Table 1 along with values calculated on the basis of the formula of the synthesised complexes. These data are in agreement with the same electrolytic behaviour of the complexes.

Magnetic properties

Oxozirconium(IV) compounds are either diamagnetic or weakly paramagnetic, depending upon the diamagnetism of the other ions and the surrounding ligand field. Their magnetic susceptibilities are independent of field strength and temperature. The ground states of oxozirconium and thorium compounds contain no unpaired electrons. The compounds are therefore weakly diamagnetic.

IR spectra and the nature of coordination (Table 2)

In the spectra of sulphoxide, two absorptions associated with S=O and C–S stretching vibrations undergo a significant shift on coordination [23]. The S=O stretching frequency in free BzSO appears as a strong absorption band at 1032 cm^{-1} while in the spectra of its complexes it is shifted to 960–950 cm^{-1}, generally appearing as a very strong broad band. The other important absorption band in the spectra of sulphoxide is the C–S stretching

TABLE 2

Pertinent IR absorption frequencies (cm^{-1}) of BzSO and its complexes with Th(IV) and ZrO(IV) [a]

Compound	Phenyl-S stretching	S=O stretching	Asym C–S stretching	Sym C–S stretching	C–S–O deformation	M–O stretching
BzSO	1079s	1032vs	682s	650w	364s 328s	–
$ThCl_4 \cdot 2BzSO$	1080s	955s	690s	665w	330s,br	400m
$ThBr_4 \cdot 2BzSO$	1075s	960s	690s 680sh	660sh	325m,br	395w
$ThI_4 \cdot 4BzSO$	1072s	960m	699s	662w	322w,br	390m
$Th(NCS)_4 \cdot 2BzSO$	1082s	955s	700s	660w	330m,br	395m
$Th(NO_3)_4 \cdot 2BzSO$	1072s	950s	697s	665w	335w,br	392m
$Th(ClO_4)_4 \cdot 6BzSO$	1075s,br	958s	702s	662w	330w	380m
$ZrOCl_2 \cdot 2BzSO$	1079s	950s	695s 670sh	660w	340m,br	390m
$ZrOBr_2 \cdot 2BzSO$	1080s	962s	690s	662w	335w,br	385m
$ZrOI_2 \cdot 2BzSO$	1075m	960m	685s	665w	325w,br	382m
$ZrO(NO_3)_2 \cdot 2BzSO$	1080s	955s	690s	670w	322w,br	400m
$ZrO(ClO_4)_2 \cdot 6BzSO$	1075s,br	960s	690s 685sh	665w 660sh	325s,br	390m
$ZrO(NCS)_2 \cdot 2BzSO$	1079s	958s	698s	665w	320m,br	395m
$ZrO(NCSe)_2 \cdot 2BzSO$	1075m	960s	700s	655w	325w,br	392m
$ZrO(BPh_4)_2 \cdot 2BzSO$	1076m	955s	705s	660w	330w,br	380m

[a] vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

absorption which has been identified in free BzSO at 682 cm^{-1}. This absorption undergoes a slight positive shift on complexation. A negative shift of the S=O stretching frequency and a shift of the C–S stretching frequency towards a higher wavenumber are indicative of the decrease in the double bond character of the S=O bond and an electron shift from the aryl group to the sulphur atom of the ligand. The data thus suggest coordination from the oxygen atom of the ligand. Several other absorptions, such as those associated with C–H stretching, C=C stretching, ring deformation mode, C–H in-plane and out-of-plane deformation modes, appear at their usual positions. These have been identified in the spectra of the complexes and have been compared with the corresponding absorption in the free ligand. As expected, no significant change is observed in their positions. A very strong absorption attributed to phenyl-S stretching by previous workers [24] has been identified at 1079 cm^{-1} in the free ligand, which does not undergo any significant change on complexation. It may be taken as an indication of the absence of coordination from the sulphur atom of the ligand. The C–S–O symmetric and antisymmetric deformation modes appear in the spectrum of the free ligand at 364 and 328 cm^{-1}, respectively, which, on complexation, incur a distinct negative shift indicating electron donation from the oxygen atom.

In the 400–380 cm^{-1} region there is a new band which is assigned tentatively as the (M–O) stretching frequency, which is comparable to that reported previously [11,12,20]. The characteristic ν(Zr=O) is observed as a weak band in the oxozirconium(IV) complex in the range 980–950 cm^{-1} [19–21].

Anions

The IR spectra of the halo complexes closely resemble each other, while the perchlorate, nitrate, thio- and seleno-cyanate and tetraphenyl boronate complexes have additional anion bands.

In both the spectra of $Th(ClO_4) \cdot 6BzSO$ and $ZrO(ClO_4)_2 \cdot 6BzSO$ the very strong ν_3 and ν_4 bands appear at ca. 1075 cm^{-1} (coupled with the phenyl-S stretching) and ca. 625 cm^{-1}, respectively, for the perchlorate ions, indicating that tetrahedral symmetry is maintained and the perchlorate ions are not bonded to the metal atom [11,12,19].

The C–N stretching frequency in all the thio- and seleno-cyanate complexes appears at ca. 2060 cm^{-1}. This C–N frequency range lies on the border line for distinguishing between sulphur and nitrogen bonding in thio- and seleno-cyanate [25], although the high relative intensity of the band in each case suggests that the thio- and seleno-cyanate groups are nitrogen bonded [26,27]. The ν(C–X) (X = S or Se) frequency observed at ca. 780 cm^{-1} and δ(NCX) at 490 cm^{-1} further confirm the N-bonding to the metal atom [28].

The absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the occurrence of two strong bands at ca. 1530 and 1300 cm^{-1} in both nitrato complexes suggest the strong covalent nature of the NO_3^- ion [29]. The bidentate nature of nitrato groups in the $Th(NO_3)_4 \cdot 2BzSO$ complex has been established by comparing the spectral bands of the complex with those of $Th(NO_3)_4 \cdot 5H_2O$ [30], where the bidentate character of the nitrato groups has been established by X-ray analysis [31]. In $Th(NO_3)_4 \cdot 2BzSO$ the NO_3^- vibrations occur at 1530 (ν_1), 1300 (ν_4), 1040 (ν_2), 815 (ν_6) and 750 cm^{-1} (ν_3/ν_5), while in $Th(NO_3)_4 \cdot 5H_2O$ the corresponding bands occur at 1520, 1290, 1030, 808, 745 and 715 cm^{-1}, respectively. In $ZrO(NO_3)_2 \cdot 2BzSO$ the NO_3 absorptions appear at 1525 (ν_1), 1290 (ν_4), 1030 (ν_2), 810 (ν_6) and 730 cm^{-1} (ν_3/ν_5). By applying the Lever separation method [32] a separation of ca. 45 cm^{-1} in the combination bands ($\nu_1 + \nu_4$) in the 1800–1700 cm^{-1} region reveals bidentate nitrate coordination.

In the spectrum of $ZrO(BPh_4)_2 \cdot 2BzSO$ the presence of four distinct strong bands at ca. 1485, 1460, 1430 and 1390 cm^{-1} indicates the coordination of tetraphenyl boronate to zirconium(IV) ion through a π-bond of the phenyl ring [33,34].

Thermal studies

A thermal review of the sulphoxide complexes of transition metals has been made by Davies and Miller [35]. However, the thermal investigations of thorium(IV) sulphoxide complexes have only been made to a limited extent. Bagnall et al. [4] studied the thermal decomposition of DMSO complexes. Vacuum TGA shows that no stable intermediate tetrachloride–DMSO complexes were observed. $ThCl_4 \cdot 5DMSO$ decomposes directly to $ThOCl_2$ (formed above 450°C), while $ThBr_4 \cdot 6DMSO$ decomposes directly to the oxydibromide $ThOBr_2$ above 400°C. Ivanova and coworkers [36,37] extended this work and thermally examined the DMSO complexes of ThX_4 ($X = Cl$, Br, I or NO_3) and ThX_2 ($X = C_2O_4$ or SO_4). All the complexes, except bidentate anions, decomposed in the temperature range 200–300°C. The oxalate and sulphate complexes lose their stability in the range 400–800°C indicating an enhanced thermal stability. ThO_2 is formed as end product in all these cases. Krishnan and Patel [11] isolated the complex $Th(ClO_4)_4 \cdot 12DMSO$ which lost six molecules of DMSO at 180°C indicating that six molecules of DMSO are either loosely bonded or held in the lattice of the crystals. $Th(ClO_4)_4 \cdot 6DMSO$ explodes at 485°C leaving behind ThO_2. The two DTA peaks are due to the overall energy effect of the endothermic heat of dissociation of $M \leftarrow O{-}S{<}$, the exothermic heat of formation of $M \leftarrow \underset{\underset{O}{\|}}{S}{<}$ and the loss of loosely held DMSO molecules in the lattice of the complex. Savant and Patel [12] reported the DTA of thorium(IV) complexes of diphenyl sulphoxide. The chloro, bromo and nitrato complexes decompose endothermically both in air and in nitrogen, while perchlorato and thiocyanato decompose exothermally in air and in nitrogen, the former decomposing violently. Agarwal and Srivastava [38] recently reported their results on the thermal studies of thorium(IV) complexes of tetramethylene sulphoxide.

The zirconyl(IV) perchlorate complex of DMSO undergoes thermal degradation according to the following equation [11]

$$ZrO(ClO_4)_2 \cdot 8DMSO \rightarrow ZrO(ClO_4)_2 \cdot 6DMSO$$

Similarly to thorium(IV) complexes of DMSO, in this complex two DMSO molecules are either loosely bonded or held in the lattice of the crystals. The complex $ZrO(ClO_4)_2 \cdot 8DPSO$, on heating at 185°C, results in the quite stable complex $ZrO(ClO_4)_2 \cdot 6DPSO$ [39], which further decomposes at 280°C, as is shown by an exothermic peak [19]. Other zirconyl(IV) complexes of DPSO have been investigated by Agarwal and Rastogi [21], and the order of stability of ZrO^{2+} complexes of DPSO is: $NO_3 > Cl > Br > NCS$. Detailed DTA of ZrO^{2+} complexes of tetramethylene sulphoxide has been reported by Agarwal et al. [20]. In all the cases ZrO_2 is produced as an end product.

TABLE 3

Thermal decomposition data for Th(IV) and ZrO(IV) complexes of dibenzyl sulphoxide

Complex	Decomp. Temp. (°C)		Decomp. product	TG weight loss (%)		DTG peak
	Initial	Final		Found	Calc.	
$ThCl_4 \cdot 2BzSO$	190	280	$ThCl_4$	53.21	55.15	endo
	410	480	$ThOCl_2$	63.96	61.75	exo
$ThBr_4 \cdot 2BzSO$	200	280	$ThBr_4$	47.32	45.45	endo
	415	470	$ThOBr_2$	61.71	59.68	exo
$Th(NCS)_4 \cdot 2BzSO$	200	270	$Th(NCS)_4$	51.98	49.78	endo
	410	450	$ThO(NCS)_2$	62.16	60.60	exo
$Th(NO_3)_4 \cdot 2BzSO$	210	280	$Th(NO_3)_4$	51.13	48.93	endo
	405	460	ThO_2	73.26	71.91	exo
$Th(ClO_4)_4 \cdot 6BzSO$	180	450	ThO_2	87.93	86.86	exo
$ZrOCl_2 \cdot 2BzSO$	210	290	$ZrOCl_2$	74.46	72.10	endo
	415	490	ZrO_2	81.92	80.72	exo
$ZrOBr_2 \cdot 2BzSO$	205	310	$ZrOBr_2$	64.26	63.27	endo
	420	480	ZrO_2	85.19	83.08	exo
$ZrO(NCS)_2 \cdot 2BzSO$	200	330	$ZrO(NCS)_2$	69.46	67.34	endo
	415	485	ZrO_2	83.42	81.99	exo
$ZrO(NO_3)_2 \cdot 2BzSO$	215	305	$ZrO(NO_3)_2$	69.16	66.57	endo
	405	475	ZrO_2	85.46	82.19	
$ZrO(ClO_4)_2 \cdot 6BzSO$	200	450	ZrO_2	93.79	92.70	exo

In the present work we describe the thermal behaviour of Th(IV) and ZrO(IV) complexes of BzSO. The thermal results are summarised in Table 3.

The TG and DTG curves of Th(IV) complexes of BzSO do not show the presence of water either in the coordination sphere or outside the coordination field. Similar to other thorium(IV) perchlorate complexes of neutral oxygen donor ligands, such as 2,6-lutidine *N*-oxide [38] or 4-aminoantipyrine [40] in the DTG curve, one sharp exothermic peak at ca. 190°C is obtained. At this temperature the compound decomposes violently due to the oxygen content of the perchlorate groups [40]. TG analysis of $Th(ClO_4)_4 \cdot 6BzSO$ shows that the complex is stable up to 180°C, beyond which the decomposition starts and is complete at ca. 450°C. At this temperature, the residual mass corresponds to ThO_2. No stable intermediate complex could be isolated in this case. In the chloro, bromo and thiocyanato complexes the decomposition process is completed in two steps. In the first step the complexes lose both the ligand molecules as shown by the break in the TG curve and the endo peak in the DTG curve. The final product is oxo halide in these cases. In the nitrato complex the two attached ligands are lost between 210 and 280°C and finally, at 460°C, metal oxide is obtained as an end product. The thermal process of the complexes indicate the following decomposition scheme.

$$Th(ClO_4)_4 \cdot 6BzSO \xrightarrow{180-450^\circ C} ThO_2$$

$$ThX_4 \cdot 2BzSO \xrightarrow{t_1} ThX_4 \xrightarrow{t_2} ThOX_2$$

for X = Cl, t_1 = 190–280°C, t_2 = 480°C; X = Br, t_1 = 200–280°C, t_2 = 470°C; X = NCS, t_1 = 200–270°C, t_2 = 450°C.

In the case of oxozirconium(IV) complexes of BzSO, the TG and DTG analyses clearly indicate the absence of water molecules in the complexes. No stable intermediate product is obtained with the $ZrO(ClO_4)_2 \cdot 6BzSO$ complex. At 450°C, ZrO_2 is obtained as the final product. In all other complexes $ZrOX_2 \cdot 2BzSO$ (X = Cl, Br, NCS, NO_3) the decomposition process is completed in two steps. In the first step both of the ligand molecules are lost and in the second step ZrO_2 is obtained as an end product. The thermal stability of these complexes fall in the order: $ClO_4 \approx NCS < Br < Cl < NO_3$.

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