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Note

INFRARED AND THERMAL STUDIES OF OXOZIRCONIUM(IV) COMPLEXES OF DIPHENYL SULPHOXIDE

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We have earlier reported the oxozirconium(IV) complexes of various oxygen donor molecules containing an X=O group (where X = C, N, S or P) [1–9]. Comparatively very little is known about the compounds of oxozirconium(IV) with sulphoxides [3,10,11]. In all the complexes, sulphoxides coordinate with ZrO(IV) through the lone oxygen atom. Diphenyl sulphoxide (DPSO) has been used as a complexing agent for various transition and non-transition metals [12–14]. The present work deals with the synthesis and characterization of complexes of DPSO with oxozirconium(IV) salts.

Lewis acids were obtained as reported previously [5,9], while DPSO was prepared in the laboratory by the reaction of pure, dry benzene with thionyl chloride in the presence of anhydrous aluminium trichloride. The metal complexes were prepared by the general method as described. A methanolic solution of the corresponding oxozirconium salt was treated with a small excess (1 : 3) of DPSO with constant stirring at 10°C. After stirring the reaction mixture for an hour, an excess of pure diethyl ether was added to the mixture and the precipitate was separated out. It was filtered, washed with methanol and finally with ether and dried in vacuo over fused $CaCl_2$.

$ZrO(BPh_4)_2 \cdot 2$ DPSO was prepared by mixing acetonic solutions of the metal salt and DPSO and leaving the reaction mixture overnight. The crystalline complex separated out and was washed with appropriate solvents and finally dried as described earlier. The selenocyanato complex of DPSO was synthesised by the method as described for other selenocyanato complexes [15].

The metal and anion analysis and physical measurements of the complexes were made as reported previously [9], while the DPSO was estimated by the standard method [16].

The analytical data of the complexes, as summarised in Table 1, show that the adducts with DPSO possess a 1 : 2 molar ratio. All the compounds

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TABLE 1

Elemental analyses and some important IR frequencies of DPSO compounds of ZrO(IV)

Compound	Zr (%)		Anion(%)		DPSO (%)		IR absorption frequencies (cm^{-1})			
	Found	Calcd.	Found	Calcd.	Found	Calcd.	ν(S=O)	ν(C–S)	ν(Zr=O)	ν(Zr–O)
DPSO							1046s	680s		
$ZrOCl_2 \cdot 2$ DPSO	15.08	15.63	11.82	12.19	67.67	69.41	970s	690s	960w	380m
$ZrOBr_2 \cdot 2$ DPSO	12.96	13.56	22.25	23.84	59.32	60.20	975s	685s	950w	390m
$ZrOI_2 \cdot 2$ DPSO	11.25	11.89	32.10	33.20	51.06	52.81	980m	685m	910w	395m
$ZrO(NO_3)_2 \cdot 2$ DPSO	14.03	14.33			62.16	63.62	960s	690s	929w	380m
$ZrO(NCS)_2 \cdot 2$ DPSO	14.19	14.51	17.80	18.50	62.32	64.43	970m	685m	930w	400m
$ZrO(NCSe)_2 \cdot 2$ DPSO	12.28	12.62			55.32	56.03	975m	682m		370m
$ZrO(BPh_4)_2 \cdot 2$ DPSO	7.03	7.91			34.46	35.16	980s	685s		380m

decomposed around 250°C. They are fairly soluble in common organic solvents. The molecular weight of the compounds, as determined cryoscopically in freezing nitrobenzene, indicates that they are monomeric in solution. The molar conductance of a 10^{-3} M solution in $PhNO_2$ is in the range 1.9–2.6 Ω^{-1} cm^2 $mole^{-1}$ indicating the absence of any ionic species.

In the IR spectra of DPSO, two absorptions associated with S=O and C–S stretching vibrations show a significant shift on coordination [17–19]. The S=O stretching frequency in free DPSO appears as a strong absorption at 1046 cm^{-1} while in the spectra of all the complexes, it has been observed in the region 980–960 cm^{-1}. The other important absorption in the spectra of sulphoxide is the C–S stretching absorption, which has been identified in free DPSO at 680 cm^{-1}. This absorption undergoes a slight positive shift on complexation. A negative shift of the S=O stretching frequency together with a positive shift of the C–S stretching frequency towards higher wave number are an indication 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. This discussion suggests coordination from the oxygen atom of the DPSO. Several other absorptions such as those associated with C–H stretching, C=C stretching, ring deformation mode, and CH in-plane and out-of-plane deformation mode appear at their usual positions. These have been identified in the spectra of the complexes and have been compared with the absorption in the free ligand (not listed). As expected no significant change is observed in their positions. A very strong absorption, attributed to phenyl–S stretching by previous workers [20], has been identified at 1089 cm^{-1} in the spectra of DPSO; since the position of this absorption 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 DPSO.

The metal–ligand vibration in these complexes has been assigned in the 400–370 cm^{-1} region [1,2,21,22].

The Zr=O characteristic band is observed in all the complexes as a weak band in the 980–910 cm^{-1} region [1,2,21,22]. In the chloro complex, Zr–Cl stretching vibrations occur at 290 cm^{-1} with a shoulder at 270 cm^{-1} [23], while the Zr–Br and Zr–I stretching vibrations could not be observed in the spectral range studied.

The absence of a ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} together with the occurrence of bands at 1510 and 1300 cm^{-1} due to the split ν_3 mode in the lower symmetry indicate the covalent nature of the nitrato group [24,25]. The two combination bands ($\nu_1 + \nu_4$) appeared as weak bands at ca. 1755 cm^{-1} and 1710 cm^{-1} in the spectra. Application of the Lever separation method [26], the separation being 45 cm^{-1} in this case, suggests the bidentate nature of the nitrato groups. The presence of bands at ca. 1035(ν_2), 800 (ν_6) and 740 cm^{-1} (ν_3/ν_5) further confirms the bidentate nature of the nitrato groups. Furthermore, the band associated with ν(Zr–O) (nitrato) is tentatively assigned at ca. 210 cm^{-1}. In thio- and selenocyanato complexes, the presence of bands in the region 2050 cm^{-1} (ν C≡N), 840 cm^{-1} (ν C–X) and 470 cm^{-1} (δ NCX) (X–S or Se) is normally associated with the terminal N-bonding thio and selenocyanato group [27]. This is quite possible since zirconium is a typical hard acid [15,28]. The N-bonding is further evidenced by a ν(Zr–N) absorption (tentatively identified) at 275 cm^{-1} for thiocyanate and 230 cm^{-1} for selenocyanate [29].

On comparing the IR spectrum of $ZrO(BPh_4)_2 \cdot 2$ DPSO with that of sodium tetraphenylboron [30,31] and other complexes of $ZrO(BPh_4)_2$ [5] in the 1500–1350 cm^{-1} region, it is found that the IR spectrum of this complex has four medium or strong bands at 1480, 1450, 1430, and 1390 cm^{-1}, which conclusively indicate the coordination of BPh_4 ions to the zirconium ion through the π-bond of a phenyl group.

The thermal investigations of the oxozirconium(IV) complexes of sulphoxides have been made to a limited extent. Patel and co-workers [10,11] have studied oxozirconium(IV) perchlorato complexes with DMSO and DPSO by DTA and TG. Agarwal et al. [3] have reported DTA of tetramethylene sulphoxide complexes of oxozirconium salts. In the present studies, chloro, bromo, thiocyanato and nitrato complexes have been selected for thermal studies.

The TG curves of the complexes do not show the presence of water molecules in the complexes. Decomposition of the halo complexes takes place in two steps. In the first step all the ligand molecules are lost and in the second step ZrO_2 is obtained as an end product [32] (Table 2). No stable intermediate product has been isolated in these cases. In the DTG curves the

TABLE 2

Thermal data on oxozirconium(IV) compounds of DPSO

Complex	Decomp. Temp. (°C)		Decomp. product	TG wt. loss (%)		DTG peak
	Initial	Final		Found	Cald.	
$ZrOCl_2 \cdot$	155	270	$ZrOCl_2$	67.32	69.41	endo
2 DPSO	340	490	ZrO_2	74.20	78.86	exo
$ZrOBr_2 \cdot$	150	290	$ZrOBr_2$	58.20	60.20	endo
2 DPSO	340	500	ZrO_2	78.52	81.66	exo
$ZrO(NCS)_2 \cdot$	145	290	$ZrO(NCS)_2$	60.36	64.43	endo
2 DPSO	350	500	ZrO_2	77.89	80.38	exo
$ZrO(NO_3)_2 \cdot$ 2 DPSO	160	190	$ZrO(NO_3)_2 \cdot$ DPSO	29.36	31.81	endo
	210	290	$ZrO(NO_3)_2$	61.90	63.62	
	330	490	ZrO_2	77.82	80.62	exo

changes have been indicated by the presence of one sharp endo peak at these temperatures and a final peak due to metal oxidation. In the nitrato complex, one ligand molecule is lost at 190°C and a stable intermediate complex with the composition $ZrO(NO_3)_2 \cdot DPSO$ has been obtained. At 290°C the remaining DPSO molecule is also lost; finally at 450°C, ZrO_2 is obtained as the final product.

In conclusion, if the minimum TG decomposition temperature is taken as a rough criterion of thermal stability, then the order of stability of ZrO^{2+} complexes of DPSO is $NO_3 > Cl > Br > NCS$.

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