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Oxozirconium(IV) Complexes of Di-*n*-Butyl and Di-*n*-Pentyl Sulphoxides

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The synthesis and physical properties of ZrO^{++} complexes of di-*n*-butylsulphoxide (DBuSO) and di-*n*-pentylsulphoxide (DPnSO) with the general composition $ZrOX_2 \cdot 2L$ ($X = Cl, Br, I, NCS, NCSe$ or NO_3 and $L = DBuSO$ or $DPnSO$) and $ZrO(ClO_4)_2 \cdot 4L$ are reported together with molecular conductivity, molecular weights and IR. In all the complexes, the sulphoxides are coordinated to zirconium(IV) through their lone oxygen atom. Thermal behaviour of the complexes has also been studied.

INTRODUCTION

In recent years, a number of oxozirconium(IV) complexes of neutral oxygen donor ligands containing $X=O$ group ($X = C, N, S$ or P) have been reported.¹ Comparatively little is known about the complexes of oxozirconium(IV) with sulphoxides.²⁻⁷ In this note the synthesis and properties of oxozirconium(IV) complexes of two alkyl sulphoxides, viz. di-*n*-butyl sulphoxide (DBuSO) and di-*n*-pentyl sulphoxide (DPnSO) are reported.

EXPERIMENTAL

All the complexes were prepared by a general method. A solution of $ZrO(IV)$ salt in methanol or acetone was treated with the respective ligand in stoichiometric ratio in the same solvent. The reaction mixture was refluxed for 2 h and the excess solvent removed by distillation. The residual mass on treatment with anhydrous diethylether yielded a crystalline solid, which was filtered, washed with ether and finally dried in vacuum over anhydrous $CaCl_2$.

The metal content of the complexes was determined as oxide. The halide content was determined by the method of Volhard and the perchlorate by Kurz's method. The electrical conductances of the complexes were measured with a Toshniwal conductivity bridge at room temperature and their molecular weights were determined cryoscopically in freezing nitrobenzene. The infrared spectra of the complexes were recorded in a $4000-200\text{ cm}^{-1}$ range using a Perkin-Elmer IR spectrophotometer, Model 521. The thermal analyses were made as reported earlier.⁸

RESULTS AND DISCUSSION

The analytical results are given in Table I. The molar conductances of the sulphoxide complexes in nitrobenzene (Table I) show that the perchlorate complexes are 1:2 electrolytes, while the halo and nitrate complexes are

non-electrolytes. This is supported by the cryoscopic molecular weights in the same solvent.

Partial IR data of the complexes are summarized in Table I. In the IR spectra of sulphoxides, two absorptions associated with S=O and C—S stretching vibrations show a significant shift on coordination.⁸⁻¹⁰ The S=O stretching frequency in free DBuSO and DPnSO appears as a strong absorption at 1046 cm⁻¹ and 1023 cm⁻¹, respectively, while in the spectra of all the complexes, it has been observed in the region 962—930 cm⁻¹. The other important absorption in the spectra of sulphoxides is the C—S stretching absorption, which has been identified in free ligands at ca. 680⁻¹. This absorption undergoes a slight positive shift upon complexation. A negative shift of the S=O stretching frequency together with a positive shift of the C—S stretching

TABLE I

Analytical, Conductivity, Molecular Weight and Partial IR data (cm⁻¹) of ZrO⁺⁺ Complexes of Sulphoxides

Compound	% Found (Calcd.)			Λ_m ohm ⁻¹ cm ² mol ⁻¹	Mol. wt. Found (Calcd.)	IR absorption frequencies cm ⁻¹		
	Zr	S	Anion			$\nu(\text{SO})$	$\Delta\nu(\text{SO})$	$\nu(\text{Zr—O})$
DBuSO	—	—	—	—	—	1046vs	—	—
ZrOCl ₂ ·2DBuSO	18.00 (18.12)	12.62 (12.74)	14.02 (14.14)	3.6	490(502)	950s	96	392m
ZrOBr ₂ ·2DBuSO	15.27 (15.39)	10.69 (10.82)	26.73 (27.07)	3.9	580(591)	960s	86	395m
ZrOI ₂ ·2DBuSO	13.18 (13.28)	9.22 (9.34)	36.60 (37.08)	4.9	676(685)	962s	84	400m
ZrO(NCS) ₂ ·2DBuSO	16.50 (16.63)	23.26 (23.40)	21.08 (21.20)	4.2	539(547)	955s	91	390m
ZrO(NCSe) ₂ ·2DBuSO	14.09 (14.19)	9.86 (9.98)	—	4.6	632(641)	960s	86	395w
ZrO(NO ₃) ₂ ·2DBuSO	16.27 (16.39)	11.42 (11.53)	—	3.8	549(555)	950s	96	390m
ZrO(ClO ₄) ₂ ·4DBuSO	9.44 (9.53)	13.29 (13.41)	20.49 (20.85)	50.9	315(954)	955s	91	395m
DPnSO	—	—	—	—	—	1023vs	—	—
ZrOCl ₂ ·2DPnSO	16.20 (16.30)	11.32 (11.46)	12.57 (12.72)	3.7	547(558)	930s	93	390m
ZrOBr ₂ ·2DPnSO	13.95 (14.06)	9.67 (9.89)	24.57 (24.72)	4.1	636(647)	935s	88	395m
ZrOI ₂ ·2DPnSO	12.18 (12.28)	8.51 (8.63)	33.82 (34.27)	4.6	729(741)	940s	83	400m
ZrO(NCS) ₂ ·2DPnSO	14.95 (15.09)	21.10 (21.22)	19.09 (19.23)	3.9	591(603)	937s	86	395m
ZrO(NCSe) ₂ ·2DPnSO	12.92 (13.05)	9.09 (9.18)	—	4.1	686(697)	940s	83	400m
ZrO(NO ₃) ₂ ·2DPnSO	14.76 (14.89)	10.36 (10.47)	—	3.6	600(611)	930s	93	390m
ZrO(ClO ₄) ₂ ·4DPnSO	8.47 (8.53)	11.89 (12.00)	18.36 (18.66)	51.3	352(1066)	940s	83	400w

frequency towards a 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 alkyl group to the sulphur atom of the ligand. Thus, it may be suggested that ZrO^{++} coordinated to the sulphoxide ligands via the lone oxygen atom.⁸⁻¹⁰ The band at 400—390 cm^{-1} has tentatively been assigned to the metal-ligand vibrations.⁵⁻⁷ The Zr=O characteristic band was observed in all complexes as a weak band in the 940—920 cm^{-1} region.⁵⁻⁷

In all the thio- and selenocyanato complexes the three fundamental frequencies $\nu(CN)$, $\nu(CX)$ and $\delta(NCX)$ ($X = S$ or Se) fall in the ranges 2080—2065, 860—810 and 480—465 cm^{-1} and clearly indicate the terminal N -bonded isothio- or isoselenocyanate to the ZrO^{++} .¹¹ In both nitrate complexes, the absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the presence of two strong bands at *ca.* 1520 and 1310 cm^{-1} attributed to ν_4 and ν_1 modes suggest the covalent nature of the nitrate groups in these complexes. The two combination bands ($\nu_1 + \nu_4$) appearing at *ca.* 1760 cm^{-1} and 1710 cm^{-1} and a separation of 50 cm^{-1} in these bands suggest the bidentate nature of nitrate groups in these complexes. The presence of ν_3 and ν_4 bands at *ca.* 1090 and 620 cm^{-1} , respectively, clearly indicate the ionic nature of the perchlorate groups.^{2,4}

Thus, it is concluded that the coordination number for zirconium in the present complexes is five or seven depending on the nature of anions.

Thermal Studies

A thermal report on ZrO^{++} complexes of sulphoxides has been published from this laboratory.⁷ Similarly to other sulphoxide complexes, the present complexes are non-hygroscopic in nature and have no water of crystallization. Halo and nitrate complexes decomposed endothermally while the perchlorato complexes decomposed exothermally with slight explosion. The weight loss values observed in the thermal decomposition of oxozirconium(IV) complexes correspond very closely with the following schemes:

- (i) $ZrOCl_2 \cdot 2L \rightarrow ZrOCl_2 \cdot 1.5L \rightarrow ZrOCl_2 \cdot 0.5L \rightarrow ZrOCl_2 \rightarrow ZrO_2$
- (ii) $ZrOX_2 \cdot 2L \rightarrow ZrOX_2 \cdot L \rightarrow ZrOX_2 \rightarrow ZrO_2$
($X = Br, NCS$ or NO_3)
- (iii) $ZrO(ClO_4)_2 \cdot 4L \rightarrow ZrO(ClO_4)_2 \rightarrow ZrO_2$

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SAŽETAK

Di-*n*-butil- i di-*n*-pentil-sulfoksidni kompleksi oksocirkonija(IV)

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Opisana je priprava u naslovu spomenutih kompleksnih spojeva općega sastava $Zr OX_2 \cdot 2L$ ($X=Cl, Br, I, NCS, NCSe, NO_3$, $L=DBuSO, DPnSO$) i $ZrO(ClO_4)_2 \cdot 4L$. U svim spojevima sulfoksidi su koordinirani na cirkonij(IV) slobodnim elektronskim parom kisikova atoma. Istraženo je termičko ponašanje pripremljenih kompleksnih spojeva.