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Note

INFRARED AND THERMAL STUDIES OF 5,6-BENZOQUINOLINE *N*-OXIDE COMPLEXES OF OXOZIRCONIUM(IV)

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We have recently reported the infrared and thermal properties of 5,6-benzoquinoline complexes of higher valent metal ions including oxozirconium-(IV) [1]. Aromatic amine *N*-oxides are potential coordinating agents [2–5]. Thus, it is worthwhile to study the coordinating ability of 5,6-benzoquinoline *N*-oxide. In the present communication, we describe the synthesis, infrared and thermal behaviour of oxozirconium(IV) complexes of 5,6-benzoquinoline *N*-oxide (Benzquo).

EXPERIMENTAL

The ligand 5,6-benzoquinoline *N*-oxide was prepared from 5,6-benzoquinoline (Merck) by the method of Ochiai [6], oxozirconium(IV) salts were synthesised using methods reported earlier [7,8].

Preparation of the complexes

All the complexes were synthesised 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 over a water bath with constant stirring. The ligand in the same solvent was added to this metal salt solution in stoichiometric ratio and the resulting mixture was refluxed for 1 h. The excess solvent was distilled off and the resulting mass was treated with excess of petroleum ether to precipitate the required complex. It was filtered, washed thoroughly with anhydrous diethyl ether and then dried in vacuo over P_4O_{10}.

All the analyses and physical measurements were done as reported earlier [8].

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RESULTS AND DISCUSSION

The interaction of oxozirconium(IV) salts with Benzquo results in the formation of complexes of the general composition $ZrOX_2 \cdot 2$Benzquo (X = Cl, Br, I, NO_3, NCS, NCSe) and $ZrO(ClO_4)_2 \cdot 4$Benzquo. The analytical data are presented in Table 1. The complexes are non-hygroscopic in nature. All the complexes are quite stable and can be stored for long periods. The complexes are partially soluble in common organic solvents. Due to the general insolubility of these complexes, we could not determine the geometry of these complexes in solution form.

The partial IR data are summarised in Table 1. The spectra do not present water bands. Considerable shifts of ν(NO), δ(NO) and γ(C–H) were observed. The shift of the N–O stretching mode to lower frequencies in relation to the free ligand indicates coordination through the oxygen [2–5]. In the perchlorate complex, the ν_3 and ν_4 bands observed at ca. 1085 and 625 cm^{-1}, respectively, indicate that they are not coordinated to the metal ion [9,10]. 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. 1520 (ν_4) and 1300 cm^{-1} (ν_1) in the spectrum of $ZrO(NO_3)_2 \cdot 2$Benzquo suggests the coordination of nitrate ions in this complex [11,12]. The two combination bands ($\nu_1 + \nu_4$) appeared as weak bands at ca. 1765 and 1720 cm^{-1} in the spectra. By applying the Lever separation method [13], a separation of 45 cm^{-1} in this case, suggests the bidentate nature of the nitrate groups. The presence of bands at ca. 1030 (ν_2), 810 (ν_6) and 735 cm^{-1} (ν_3/ν_5) further confirms the

TABLE 1

Analytical and spectral data for oxozirconium(IV) complexes

Complex	%Metal found (calc.)	%Nitrogen found (calc.)	%Anion found (calc.)	ν(N–O) (cm^{-1})	δ(N–O) (cm^{-1})	ν(Zr–O) (cm^{-1})
Benzquo	–	–	–	1235vs 1240sh	840s	–
$ZrOCl_2 \cdot 2$Benzquo	15.91 (16.02)	4.79 (4.92)	12.32 (12.50)	1220s	835s	450m
$ZrOBr_2 \cdot 2$Benzquo	13.72 (13.85)	4.11 (4.26)	24.01 (24.35)	1225s	830m	400m
$ZrOI_2 \cdot 2$Benzquo	12.01 (12.11)	3.64 (3.72)	33.16 (33.82)	1220s	832m	390m
$ZrO(ClO_4)_2 \cdot 4$Benzquo	8.36 (8.49)	5.10 (5.22)	18.24 (18.58)	1225s	835m	395m
$ZrO(NO_3) \cdot 2$Benzquo	14.53 (14.65)	8.89 (9.01)	– –	1218s	830m	400m
$ZrO(NCS)_2 \cdot 2$Benzquo	14.72 (14.84)	8.91 (9.13)	8.91 (9.13)	1220s	835m	395m
$ZrO(NCSe)_2 \cdot 2$Benzquo	12.74 (12.87)	7.78 (7.92)	– –	1225s	835m	390m

bidentate nature of the nitrate groups [14]. The IR spectra of thio- and selenocyanate complexes indicate the presence of bands in the region of 2070 (νC≡N), 860 (νC–X) and 475 cm^{-1} (δNCX) (X = S, Se), which is normally associated with the terminal N-bonding thio- and selenocyanato group [15,16]. This is quite possible since zirconium is a typical hard acid [17]. In the far-IR region, metal–ligand vibrations have been identified in the 405–390 cm^{-1} region [18,19].

Thermal studies

We have already reported the thermal properties of a number of oxozirconium(IV) complexes with some aromatic *N*-oxides [18–20]. In the present investigation, only chloro, bromo, perchlorato, nitrate and thiocyanato complexes of Benzquo have been taken for study. Thermoanalytical results are summarised in Table 2. TG curves clearly confirm the view that the complexes are non-hygroscopic in nature and have no water of crystallization either in or out of the coordination sphere. The low temperature decomposition of the iodo complex (ca. 135°C) indicates the presence of loosely held iodo ligands. Except perchlorato complexes all the other complexes decompose endothermically, while the perchlorato complex decompo-

TABLE 2

Thermoanalytical results of oxozirconium(IV) complexes

Compound	Decomposition temp.		Decomposition product	TG loss (wt.%)		DTA peak
	Initial	Final		Found	Calc.	
$ZrOCl_2\cdot$ 2Benzquo	210	290	$ZrOCl_2\cdot$Benzquo	35.72	(34.33)	endo
	320	365	$ZrOCl_2$	69.29	(68.66)	
	450	590	ZrO_2	80.12	(78.34)	
$ZrOBr_2\cdot$ 2Benzquo	200	285	$ZrOBr_2\cdot$Benzquo	30.79	(29.68)	endo
	330	370	$ZrOBr_2$	62.63	(59.36)	
	460	590	ZrO_2	82.91	(81.27)	
$ZrO(ClO_4)_2\cdot$ 4Benzquo	195	280	$ZrO(ClO_4)\cdot$2Benzquo	38.18	(36.41)	exo
	325	370	$ZrO(ClO_4)_2$	74.16	(72.82)	
	460	595	ZrO_2	90.12	(88.51)	
$ZrO(NO_3)_2\cdot$ 2Benzquo	230	295	$ZrO(NO_3)\cdot$Benzquo	32.91	(31.40)	endo
	330	375	$ZrO(NO_3)_2$	64.16	(62.80)	
	455	595	ZrO_2	82.90	(80.19)	
$ZrO(NCS)_2\cdot$ 2Benzquo	200	290	$ZrO(NCS)_2\cdot$Benzquo	33.12	(31.81)	endo
	325	370	$ZrO(NCS)_2$	65.16	(63.62)	
	450	595	ZrO_2	91.16	(79.93)	

ses exothermically and smoke is formed during the decomposition. The thermal process of the complex indicates the decomposition scheme

$$ZrOX_2 \cdot 2Benzquo \xrightarrow{t_1} ZrOX_2 \cdot Benzquo \xrightarrow{t_2} ZrOX_2 \xrightarrow{t_3} ZrO_2$$

X	t_1 (°C)	t_2 (°C)	t_3 (°C)
Cl	210–290	320–365	590
Br	200–285	330–370	590
NO_3	230–295	330–375	595
NCS	200–290	325–370	595

$$ZrO(ClO_4)_2 \cdot 4Benzquo \xrightarrow{195-280°C} ZrO(ClO_4)_2 \cdot 2Benzquo \xrightarrow{325-370°C} ZrO(ClO_4)_2 \xrightarrow{595°C} ZrO_2$$

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