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Note

INFRARED AND THERMAL INVESTIGATIONS OF TIN(IV) HALIDE COMPLEXES OF 5,6-BENZOQUINOLINE *N*-OXIDE AND 1,10-PHENANTHROLINE *N*,*N*′-DIOXIDE

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In continuation of our work on tin(IV) complexes of aromatic amine *N*-oxides [1], now we report the infrared and thermal properties of tin(IV) complexes of 5,6-benzoquinoline *N*-oxide (Benzquo) and 1,10-phenanthroline *N*,*N*′-dioxide ($PhenNO_2$).

EXPERIMENTAL

Tin tetrachloride (Fischer certified grade), tetrabromide and iodide (BDH) were used without further purification. The ligand 5,6-benzoquinoline *N*-oxide was prepared from 5,6-benzoquinoline by the method of Ochiai [2], while 1,10-phenanthroline *N*,*N*′-dioxide was prepared by the method described for 2,2′-bipyridyl *N*,*N*′-dioxide [3,4].

Preparation of the complexes

The molecular adducts mentioned herein were prepared by direct interaction of tin tetrahalides with ligands according to the following equation

$$SnX_4 + nL \rightarrow SnX_4 \cdot nL$$

($X = Cl, Br, I$; $n = 1, 2$).

The reaction products were isolated by one of the following two methods.

(a) In a typical experiment, 2.5 mmol of tin tetrahalide in chloroform were mixed with a solution of 5 mmol of the ligand in ethanol. A vigorous reaction accompanied by liberation of heat took place. The precipitated solid was filtered, washed several times with ethanol and diethyl ether and dried in vacuum.

(b) In a typical experiment, 2.5 mmol of tin tetrahalide in chloroform were mixed with a solution of 5 mmol of the ligand in ethanol and the mixture was refluxed for 2–3 h. The excess solvent was distilled off and the resulting viscous mass was treated with excess of petroleum ether or diethyl ether to precipitate the required complex. The product was washed with the precipitating solvent and dried in vacuum.

Tin was estimated by heating a known weight of the compound, with a mixture of concentrated sulphuric acid and fuming nitric acid in a weighed silica crucible and determining the amount of stannic oxide formed. All other physico-chemical measurements of the complexes were made as reported previously [5].

RESULTS AND DISCUSSION

The analytical data collected in Table 1 show that the adducts with 5,6-benzoquinoline *N*-oxide are of 1 : 2 stoichiometry whereas those with 1,10-phenanthroline *N*,*N*′-dioxide, which is a bidentate ligand, are of 1 : 1 stoichiometry. The complexes generally have high melting points and mostly decompose at their melting point. The chloride complexes are white whereas those of bromide and iodide are of pale-yellow and orange colour, respectively. They are soluble in organic solvents such as nitromethane, nitrobenzene and methylene chloride and are non-hygroscopic in nature. The conductance of these complexes was determined in nitrobenzene. As the results are almost similar and indicate the absence of ionic species, it is considered of little interest to describe the data. The molecular weights of the complexes determined cryoscopically in nitrobenzene show that the complexes are monomeric and do not appreciably dissociate in solution.

TABLE 1

Analytical, conductivity, molecular weight and IR data (cm^{-1}) for tin(IV) compounds

Compound	Found (calcd.)(%)			Λ_m ($ohm^{-1} cm^2 mol^{-1}$)	Formula weight	ν(N–O)	ν(Sn–O)
	Sn	N	Halogen				
Benzquo	–	–	–	–	–	1235vs	–
						1240sh	
$SnCl_4 \cdot 2$Benzquo	18.42	4.21	21.62	3.4	651	1225s	382m
	(18.27)	(4.30)	(21.81)			1220s	
$SnBr_4 \cdot 2$Benzquo	14.51	3.19	38.43	3.9	829	1228s	370m
	(14.35)	(3.37)	(38.60)			1225s	
$SnI_4 \cdot 2$Benzquo	11.91	2.62	49.79	4.7	1017	1230s	362m
	(11.70)	(2.75)	(49.95)			1225s	
$SnCl_4$	–	–	–	–	–	1312s	–
						1282s	
$SnCl_4 \cdot PhenNO_2$	25.00	5.75	29.84	3.2	473	1280s	385m
	(25.15)	(5.91)	(30.02)			1265m	
$SnBr_4 \cdot PhenNO_2$		4.18	48.98	4.1	651	1290s	365m
	(18.27)	(4.30)	(49.15)			1270m	
$SnI_4 \cdot PhenNO_2$		3.20	60.36	4.9	839	1290m	355m
	(14.18)	(3.33)	(60.54)			1280m	

Infrared spectral studies and mode of coordination

Benzquo complexes

The IR spectra of the complexes show that the N–O stretching vibration of the ligand occurs as strong absorption at 1235 cm^{-1} with a shoulder at 1240 cm^{-1}, which are shifted to a lower frequency in the 1230–1220 cm^{-1} region (Table 1). This indicates the coordination of the ligand through the lone oxygen of the N–O group [6,7]. The NO bending vibration of the Benzquo is assigned as a strong band at ca. 840 cm^{-1} and only a slight shift of this vibration is observed on complexation [6,7]. This is further support of metal–oxygen coordination. The positive shift of the C–H out-of-plane vibration of the ligand in all the complexes is indicative of the drainage of electron density from the pyridine ring to the metal ion.

PhenNO$_2$ complexes

In the IR spectra of free ligand, two N–O bands have been observed at 1312 and 1282 cm^{-1}. These bands have been observed to shift to lower frequencies upon complex formation. The decrease in the frequency of the ν(N–O) vibration is attributed to *O,O*-chelation [8,9] (Table 1). The NO bending appears at 880 and 845 cm^{-1}. In the present complexes δ(NO) appears in the region 860–840 cm^{-1}, this is further support of the *O,O*-chelation. A positive shift has been observed in the vibrations associated with C–H out-of-plane deformation, which is due to tightening of the aromatic ring on complexation [6,7].

Far-IR region

In the region 400–300 cm^{-1} there is a characteristic strong band, the frequency of which is comparable to the Sn–O (metal–ligand) stretching frequency observed in various oxygen-donor ligand complexes of tin(IV) [10,11]. As shown in Table 1 the displacement of the band to higher frequency with increasing electronegativity of the halogen indicates a progressive increase in the Sn–O bond strength. In comparison to this, shifts in N–O stretching frequencies do not necessarily reflect variations in the Sn–O bond strength so directly, particularly since the effects produced by charge withdrawal and by kinematic coupling of the ligand and Sn–O vibrations act in opposition [12].

Tin–halogen stretching frequencies are very sensitive to changes in the coordination number of the tin atom. Thus, in tin tetrachloride, the Sn–Cl stretching vibration appears at 403 cm^{-1} and in $SnCl_4 \cdot$2Benzquo and $SnCl_4 \cdot$PhenNO$_2$ the Sn–Cl stretching vibrations occur at 330 and 325 cm^{-1}, respectively. A negative shift is thus observed indicating a definite increase in coordination number of the tin atom. As a splitting of the Sn–Cl stretching vibration is distinctly observed in the complexes, it may be concluded that the ligand molecules occupy *cis* positions in the octahedral

TABLE 2

Thermal decomposition data for Sn(IV) complexes of amine *N*-oxides

Complex	Decomp. temp. (°C)		Decomp. product	TG wt. loss (%)		DTA peak
	Initial	Final		Found	Calcd.	
$SnCl_4 \cdot 2$Benzquo	215	265	$SnCl_4 \cdot$Benzquo	31.15	29.95	endo
	280	330	$SnCl_4$	61.85	59.90	exo
	360	515	SnO	78.52	76.80	
$SnBr_4 \cdot 2$Benzquo	205	250	$SnBr_4 \cdot$Benzquo	25.15	23.52	endo
	275	320	$SnBr_4$	48.55	47.04	exo
	350	510	SnO	83.15	81.78	
$SnCl_4 \cdot PhenNO_2$	190	210	$SnCl_4 \cdot 0.4PhenNO_2$	28.10	26.89	endo
	270	320	$SnCl_4$	46.25	44.82	exo
	355	510	SnO_2	69.85	68.07	
$SnBr_4 \cdot PhenNO_2$	185	205	$SnBr_4 \cdot 0.4PhenNO_2$	20.85	19.53	endo
	260	310	$SnBr_4$	34.10	32.56	exo
	350	505	SnO_2	78.10	76.80	

symmetry in all complexes. The data support the conclusion arrived at earlier on the basis of the splitting of the N–O stretching vibration.

Thermal studies

The thermal properties of tin(IV) complexes of aromatic amine *N*-oxides have only been studied to a limited extent [1]. The results of thermal analyses are summarised in Table 2. The TG and DTA curves of the present complexes do not show the presence of water molecules either in or out of the coordination sphere. Thermograms of the complexes show the following decomposition scheme

$$SnX_4 \cdot 2\text{Benzquo} \rightarrow SnX_4 \cdot \text{Benzquo} \rightarrow SnX_4 \rightarrow SnO$$

$$SnX_4 \cdot PhenNO_2 \rightarrow SnX_4 \cdot 0.4PhenNO_2 \rightarrow SnX_4 \rightarrow SnO$$

In the DTA curve, only two peaks have been observed. First, an endothermic peak due to decomposition of the complexes. At this stage all the ligand molecules have been lost. Second, an exothermic peak, due to metal oxidation. On the basis of the decomposition temperature, it is concluded that chloro complexes are more thermally stable than bromo complexes.

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