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Note

INFRARED AND THERMAL STUDIES OF TIN(IV) HALIDE COMPLEXES OF SUBSTITUTED AMINO PYRIDINE *N*-OXIDES

R.K. AGARWAL and H.K. RAWAT

Department of Chemistry, Lajpat Rai (P.G.) College, Sahibabad 201 005, Ghaziabad (India)

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A number of workers [1–10] have reported on the aromatic amine *N*-oxide complexes of tin(IV). Halogens are common ligands in coordination chemistry, readily forming coordinate bonds with metals. However, not much is known about tin(IV) halide complexes of the N–O donor system. Therefore, this note describes the preparation, IR spectra and thermal decomposition characteristics of the coordination compounds formed by the interaction of tin(IV) halides with 2-methyl and 2-dimethyl amino pyridine *N*-oxides.

EXPERIMENTAL

Tin tetrachloride (Fischer's certified grade), tetrabromide and iodide (BDH) were used without further purification. 2-Methyl amino pyridine *N*-oxide (MAPO) and 2-dimethyl amino pyridine *N*-oxide (DMPO) were prepared from 2-amino pyridine by the method of Katritzky [11].

The metal ion complexes were prepared by the following general method. Tin tetrahalide (2.0 mmol) in absolute ethanol (10 ml) was mixed with a solution of the ligand (4.0 mmol) in the same solvent (20 ml) and the mixture was refluxed for 2–3 h. The excess solvent was distilled off and the residual viscous mass was treated with an excess of diethyl ether to precipitate the desired complex. The product was washed and dried in vacuo over P_4O_{10} (yield, ca. 60–70%).

The elemental analyses were carried out by standard semi-micro techniques. Other physico-chemical measurements of the complexes were made as reported previously [12].

RESULTS AND DISCUSSION

The analytical data recorded in Table 1 indicate that the interaction of Sn(IV) halide with amine *N*-oxides results in the formation of complexes of the type $SnX_4 \cdot 2L$. The chloride complexes are white crystalline solids,

TABLE 1

Analytical, conductivity and molecular weight data for tin(IV) compounds

Complex	Found (calcd.) (%)					Ω_m (ohm^{-1} cm^2 mol^{-1})	Formula weight
	Sn	C	H	N	Halogen		
$SnCl_4 \cdot 2MAPO$	23.69	28.42	3.08	10.81	27.52	2.2	509
	(23.37)	(28.29)	(3.14)	(11.00)	(27.89)		
$SnBr_4 \cdot 2MAPO$	17.56	21.16	2.26	8.02	46.16	2.8	687
	(17.32)	(20.96)	(2.32)	(8.15)	(46.57)		
$SnI_4 \cdot 2MAPO$	13.82	16.62	1.74	6.21	57.42	3.9	875
	(13.60)	(16.45)	(1.82)	(6.40)	(58.05)		
$SnCl_4 \cdot 2DMPO$	22.32	31.42	3.63	10.19	26.16	2.5	537
	(22.16)	(31.28)	(3.72)	(10.42)	(26.44)		
$SnBr_4 \cdot 2DMPO$	16.81	23.61	2.58	7.69	44.22	2.9	715
	(16.64)	(23.49)	(2.79)	(7.83)	(44.75)		
$SnI_4 \cdot 2DMPO$	13.32	18.82	2.06	6.02	55.72	3.8	903
	(13.17)	(18.60)	(2.21)	(6.20)	(56.25)		

whereas those of bromide and iodide are pale yellow and orange in colour, respectively. All the complexes possess high melting points and mostly decompose at their melting point. The complexes are soluble in organic solvents such as chloroform, acetonitrile and nitrobenzene, and are unaffected by atmospheric moisture. The molecular weights of the complexes determined cryoscopically in nitrobenzene show that they are monomeric in solution. The molar conductances of a 10^{-3} M solution in nitrobenzene are in the range 2.2–3.9 Ω^{-1} cm^2 mol^{-1}, indicating the absence of ionic species.

Infrared spectral studies

The ligands MAPO and DMPO are the substituted 2-amino pyridine *N*-oxide, which have two potential donor sites in the *N*-oxygen and *N*-alkyl groups. Thus, as the neutral molecules, the ligands act as monodentate bonding through either the *N*-oxygen or *N*-alkyl groups, or bidentate bonding through both the coordinating sites. Katritzky and Hands [13] have examined the IR spectra of the heterocyclic ring vibrations of a large number of 2-substituted pyridine *N*-oxides, including 2-methyl and 2-dimethyl amino pyridine *N*-oxides. West and co-workers [14–16] have reported on a number of metal complexes of these ligands. Table 2 records important IR bands for the ligands and the tin(IV) complexes.

In the spectra of the ligands examined, an absorption of very strong intensity in the range 1205–1220 cm^{-1} has been assigned to the NO stretching vibration mode. It undergoes a significant negative shift $(-\Delta\nu(NO) = 20\text{–}25$ cm$^{-1})$ on complexation [14–16]. The decrease in frequency is attributed to coordination from the oxygen atom of the base

TABLE 2

Partial IR spectral data (cm^{-1}) of tin(IV) compounds

Compound	ν(N–O)	δ(N–O)	ν(C–H) out of plane	ν(Sn–O)
MAPO	1205s	850m	765s	–
$SnCl_4 \cdot 2MAPO$	1190s 1180sh	840m	772s	390m
$SnBr_4 \cdot 2MAPO$	1192s 1185sh	842m	770s	380m
$SnI_4 \cdot 2MAPO$	1192s 1180sh	843m	769s	360m
DMPO	1220s	840s	765s	–
$SnCl_4 \cdot 2DMPO$	1205s 1200sh	832s	772s	385m
$SnBr_4 \cdot 2DMPO$	1200s 1190m	835s	770s	375m
$SnI_4 \cdot 2DMPO$	1200sh 1190m	835s	770s	362m

s, strong; m, medium; sh, shoulder.

causing a decrease in π-character of the N–O bond. The NO bending has been assigned to 840 cm^{-1} and, from the tabulated data, it is apparent that only a slight shift of this vibration is obesrved on complexation. The absorptions associated with C–H out-of-plane deformation modes are supposed to undergo a slight positive shift due to tightenining of the aromatic ring on complexation. A positive shift of ca. 10 cm^{-1} has been observed in this mode of vibration which is in conformity with the observations of earlier workers [14–16]. The vibrations attributed to the methylamino or dimethylamino groups are only slightly changed in the complexes as compared to the ligand.

In the far-IR region, there is a characteristic medium band in the range 390–360 cm^{-1} which is assigned to the Sn–O stretching mode on the basis of reports on various complexes of tin [17,18]. The displacement of the bond to a higher frequency with increasing electronegativity of the halogen indicates a progressive increase in the Sn–O bond strength. Thus, it is concluded that these ligands act as monodentate bonding through the oxygen atom. Since the ν(NO) vibration undergoes splitting on complexation, this may be taken as an indication that the two ligand molecules occupy *cis*-positions in the complexes possessing octahedral geometry [19].

Tin–halogen stretching frequencies are 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} while it occurs at ca. 310 cm^{-1} in both the chloro complexes reported here, which is indicative of an increase in the coordination number of the tin atom. ν(Sn–Br) and ν(Sn–I) could not be assigned because they do not fall within the range of the present study.

TABLE 3

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

Complex	Decomp. temp. (°C)		Decomp. product	TG wt. loss		DTG temp. (°C)
	Initial	Final		Found (%)	Calcd. (%)	
$SnCl_4 \cdot 2MAPO$	205	250	$SnCl_4 \cdot MAPO$	25.62	24.36	
	265	310	$SnCl_4$	51.39	48.72	290 endo
	360	510	SnO_2	72.16	70.33	490 exo
$SnBr_4 \cdot 2MAPO$	195	235	$SnBr_4 \cdot MAPO$	20.39	18.04	280 endo
	260	305	$SnBr_4$	38.21	36.09	480 exo
	350	505	SnO_2	80.16	78.02	
$SnCl_4 \cdot 2DMPO$	210	255	$SnCl_4 \cdot DMPO$	27.12	25.69	
	265	295	$SnCl_4$	53.61	51.39	285 endo
	330	510	SnO_2	74.06	71.88	490 exo
$SnBr_4 \cdot 2DMPO$	200	240	$SnBr_4 \cdot DMPO$	20.57	19.30	275 endo
	270	295	$SnBr_4$	40.12	38.60	485 exo
	350	505	SnO_2	80.36	78.88	

THERMAL STUDIES

Thermal investigations of various metal complexes with some aromatic amine *N*-oxides have already been made by a number of workers [20–22]. However, much less is known about the thermal behaviour of tin (IV) halide complexes of aromatic amine *N*-oxides. Therefore, it was thought worthwhile to extend the thermal investigation to the tin(IV) halide complexes.

The results of thermal analyses are summarised in Table 3. All the complexes are non-hygroscopic in nature and decompose in three steps which may be shown as

$$SnX_4 \cdot 2L \rightarrow SnX_4 \cdot L \rightarrow SnX_4 \rightarrow SnO_2$$

These changes in the DTG curves are apparent by two peaks: first, the endo peak, which indicates the total loss of ligands at this temperature; second, the exo peak, which is due to metal oxidation. On the basis of decomposition temperatures, it is concluded that chloro complexes are more thermally stable than bromo complexes.

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