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THERMOANALYTICAL STUDIES ON ANTIMONY(III) COMPLEXES WITH MONOCHLOROBENZOYLHYDRAZONES OF 2-FURALDEHYDE(FpClBHH),2-PYRROLALDEHYDE (PmClBHH) AND 2-THIOPHENALDEHYDE(TpClBHH) AS LIGANDS

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ABSTRACT

The antimony(III) trihalides,SbX_3(X=Cl,Br and I) react with the title ligands to give the compounds SbX_3L (L=p-chlorobenzoylhydrazones of 2-Furaldehyde(FpClBHH) 2-Pyrrolaldehyde (PmClBHH) and 2-Thiophenaldehyde(TpClBHH). The characterization of the new species was based on their elemental analysis,spectral data(IR,UV-Vis) as well as on thermal studies. The ligands appear to offer two coordination sites -the carbonyl and azomethine group- and perhaps a third one -the heteroatom of the heterocyclic ring. The structures proposed for the investigated complexes are either pseudo- or distorted octahedral.

INTRODUCTION

In the course of our studies we reported (1-7) the results on the synthesis and characterization of Sn(II),Ni(II),Ti(IV),Pt(II),Pd(II),Rh(III),Zn(II),Cd(II) and Hg(II) complexes employing as ligands monochlorobenzoylhydrazones.

Herein we present the preparation and study of Sb(III) complexes with the title ligands.

EXPERIMENTAL

The ligands were prepared by literature methods (8). All chemicals were reagent grade and used without further purification. The thermoanalytical investigations were carried out with a Mettler TA 2000 system equipped with Metrowatt SE 460 recorder . A sample weight ca. 20 mg was used and the heating rate was 10 deg/min. A dynamic N_2 atmosphere was applied in all cases, to avoid oxidation of the sample. The complexes were prepared according to the following general procedure:

Equal volumes (10 ml) of equimolar (1 mmol) solutions of hydrazone and an antimony(III) trihalide in dry methanol were mixed, and the resulting solution was stirred for 1 h at room temperature. It was then concentrated to half to its volume affording a residue. The solid was removed by suctional filtration, washed with diethylether (2X10 ml) and dried in vacuo.The procedure could be accomplished in considerable less time by warming the reaction mixture at 40-60°C. All the new compounds could be recrystallised from warm methanol.

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RESULTS AND DISCUSSION

Treatment of antimony(III) halides with the title ligands in 1:1 molar ratio in dry methanol, resulted in formation of the mentioned complexes.The new compounds are microcrystalline solids, stable in dry air.

The absorption maxima of the studied complexes in methanol solutions are listed in Table 1. The two intense absorption bands falling in the ranges of 220-270 and 312-318 nm are due to intra-ligand transitions of $\pi^*\leftarrow\pi$ and $\pi^*\leftarrow n$ type, located mainly on the C=N and C=O groups, respectively (9).

Bands occuring in the region 480-580 nm of complexes may be assigned to ligand-to-metal charge transfer transition, which are considered responsible for the colour of the compounds. The IR spectra are more informative about the possible coordination sites of the investigated ligands than the UV-Vis ones. In particular,the IR spectra of the compounds show bands due to ν(C=O) group,being at lower frequencies as compared with those of the free ligands (10-12). The lowering lies between 15 and 75 cm^{-1} designating in this way that the C=O group is one of the coordination sites of the ligands. The absorption bands attributed to >C=N stretching frequency in pure hydrazones have shifted to lower spectral region by 15 to 65 cm^{-1}, indicating that the nitrogen of the azomethine moiety is the second coordination site (10-13). The existence of bands assigned to ν(Sb-O) and to ν(Sb-N) (Table 1) is a further support to the above arguments. Taking into account the above IR data as well as the analytical results of all complexes one can presume a pseudooctahedral structure for them. However, the existence of bands in the region 375-345 cm^{-1} in the IR spectra of complexes with p-chlorobenzoylhydrazone of 2-thiophenaldehyde which can be assigned to ν(Sb-S), is an indication that the ligands may offer the heteroatom (O,N,S) of the heterocyclic ring as a third coordination site.

Taking also into consideration the known tendency of antimony(III) to achieve hexa-coordination in its complexes (10), we can conclude that the new compounds may acquire distorted octahedral structures.

TG, DTG and DTA data for the Sb(III) complexes and corresponding temperature ranges, mass losses and residue masses are summarised in Table 2.

Generally, the thermal decomposition of the investigated complexes proceeds via 1 or 3 stages; the number of such stages may depend on the nature of the hydrazone and of the halogen involved.

The TG profile of $SbCl_3$·FpClBHH shows three consecutive steps. The first step corresponds to the evolution of a chlorine atom, whereas the second and the third ones indicate the removal of the FpClBHH ligand and the loss of further two chlorine atoms, respectively.The experimentally found percentage of the final residue (25%) is very close to the calculated one (25.54%), if it is considered to be elemental antimony (14).

Table 1. The most Relevant Infrared and UV-Vis Bands of the New Sb(III) Complexes.

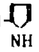
	$SbCl_3$·FpClBHH	$SbCl_3$·TpClBHH	$SbBr_3$·TpClBHH	SbI_3·TpClBHH	SbI_3·PmClBHH
a. Infrared Bands [cm^{-1}]					
ν(C=O)	1630 vs*	1600 vs	1590 vs	1580 vs	1605 vs
ν(N-N)	945 s	930 w	925 w	925 w	920 w
ν(Sb-N)	545 m	530 m	500 w	530 w	530 w
ν(Sb-O)	430 w	420 m	415 w	415 w	420 w
ν(Sb-X)	330 m	320 s	290 w	-	-
	305 s	310 s			
ν(Sb-S)	-	360 s	355 m	345 m	-
b. UV-Vis Bands [nm (logε)]					
	236(4.19)	242(4.32)	241 sh	220(4.83)	268(4.38)
	312(4.53)	265(4.32)	268(4.44)	270(4.90)	315(4.34)
		318(4.70)	318(4.53)	318(4.52)	480(3.70)
					580(3.86)

* vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

As far as the complexes $SbCl_3$·TpClBHH and $SbBr_3$·TpClBHH are concerned, their thermoanalytical curves exhibit only one step, consequently, they appear to lose one ligand and three halogens simultaneously. However, the DTG curve of the latter shows a peak and a shoulder at 315 and 355^{o}C, respectively; the former corresponds to the loss of one ligand and a halogen, whereas the latter to the evolution of two halogens. The percentage of the residue left for $SbBr_3$·TpClBHH is almost the same with the calculated one, whereas the percentage for $SbCl_3$·TpClBHH is much lower than the expected one.

The TG curves of SbI_3·TpClBHH and SbI_3·PmClBHH do not display well defined stages and their other thermoanalytical data are not very informative about their way of degradation. In particular, the thermal decomposition of SbI_3·TpClBHH should be more complicated because its DTA curve shows many peaks, mainly exothermic, in comparison with all the other complexes in question. On the other hand its TG curve shows that it appears to loose one ligand and two iodine atoms in one step or one ligand and three halogens in the first two stages. The complex SbI_3·PmClBHH seems to loose two iodine atoms and one ligand in three

Table 2. DTA/TG/DTG Data for Sb(III) Complexes

Compound	DTA results Peak temperature (°C) *endothermic* (-) exothermic (+)	Stage	TG/DTG results Temperature range (°C)	 DTG_{max} (°C)	 Mass loss (%)	 Evolved moiety formula	 Mass calculated (%)
$pClC_6H_4CONHN{=}CH$-  $\cdot SbCl_3$	190 (-)	a	145-195	190	6.5	Cl	7.44
	223 (+)	b	195-292	255	50.8	{ $pClC_6H_4CONHN{=}CH$-  }	52.16
		c	292-610		17.7	2Cl	14.87
		residue			25.0	Sb	25.54
$pClC_6H_4CONHN{=}CH$-  $\cdot SbCl_3$	197.5 (-)	a	230-410	331	83.5	{ $pClC_6H_5CONHN{=}CH$-  +3Cl}	75.29
		residue			16.5	Sb	24.70
$pClC_6H_4CONHN{=}CH$-  $\cdot SbBr_3$	192.5 (-)	a	190-390	315	80.8	{ $pClC_6H_5CONHN{=}CH$-  +3Br}	80.54
		residue		355	19.2	Sb	19.44
$pClC_6H_4CONHN{=}CH$-  $\cdot SbI_3$	190 (-) 230 (-)	a	172-345		70.0	{ $pClC_6H_5CONHN{=}CH$-  +2I}	67.58
	315 (+) 480 (+)	b	345-490		11.6	I	16.54
	585 (+) 625 (+)	c	490-660		12.7	?	
	652 (+)	residue			5.7	?	15.87
$mClC_6H_4CONHN{=}CH$-  $\cdot SbI_3$	248 (+)	a	137-215	177	5.9	I	16.92
	627 (-)	b	215-495	295	50.1 } 68.7	{ $mClC_6H_5CONHN{=}CH$-  }	33.01 } 66.85
		c	495-725°C	382	12.7	I	16.92
		residue		443	31.3	Sb+I	33.15

overlapping steps. The percentage of the residue left for both complexes is much lower than the expected one for SbI_3·TpClBHH, whereas it is slightly lower for $SbCl_3$·PmClBHH.

In conclusion, the thermal investigation of the studied complexes showed that only the decomposition of $SbCl_3$·FpClBHH proceeds in a rather smooth and understandable way. The TG curves of the rest compounds show decompositions occurring either in one step or in three overlapping steps. This situation may be due either to the physical condition of the decomposing solid, which may not allow easily to escape the evolved moieties, or to the volatility of the halogen involved. The latter could mean that the evolution of a certain halogen could take place in two consecutive steps, therefore making them overlapping. Perhaps, a combination of the two factors may play the most important part in the decomposition of the investigated complexes.

The mass spectra of all complexes show no peaks due to molecular ions, whereas fragments of the ligands involved were detected as well as some halogenated species of antimony(III), $[SbX_n]^+$ (X=Cl,Br and I; n=1-3).

From the available thermoanalytical data as well as those obtained from the mass spectra we propose the following decomposition reactions for all complexes:

1st step $SbX_3L \rightarrow SbX_2L + X$

2nd step $SbX_2L \rightarrow SbX_2 + L$

3rd step $SbX_2 \rightarrow Sb + 2X$

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