MONOHALOGENOBENZOYLHYDRAZONES VI.
NEW ANTIMONY(III) COMPLEXES
WITH MONOCHLOROBENZOYLHYDRAZONES
OF 2-FURALDEHYDE, 2-PYRROLALDEHYDE
AND 2-THIOPHENALDEHYDE AS LIGANDS

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The antimony(III) trihalides, SbX_3 (X = Cl, Br and I), react with the title ligands to give the compounds SbX_3L, where L = benzoyl- and monochlorobenzoylhydrazones of 2-furaldehyde (FBHH and FClBHH), 2-pyrrolaldehyde (PBHH and PClBHH) and 2-thiophenaldehyde (TBHH and TClBHH). The characterization of the new species was based on their elemental analyses, spectral data (IR and UV–Vis) and thermal studies. The ligands appear to offer two coordination sites (the carbonyl and azomethine groups) and perhaps a third one (the heteroatom of the heterocyclic ring). The thermal decompositions of the studied complexes proceed via one or three stages, the number of stages depending on the nature of both the hydrazones and the halogens. The structures proposed for the investigated complexes are either pseudo- or distorted octahedral.

Our project concerning the complexes of monohalogenobenzoylhydrazones started several years ago. In the course of this work we have prepared and studied the Sn(II) [1] and Ni(II) [2] complexes, as well as those of the IIB subgroup metals [3]. After these first attempts, our interest focused on the synthesis of Ti(IV) complexes, and a distorted octahedral structure was accepted around the titanium atom [4]. In order to test the coordination ability of the monohalogenobenzoylhydrazones towards metals from other parts of the periodic Table, we tried reactions with Pt(II), Pd(II), Rh(III) and Sb(III). The former metals gave several interesting compounds; their synthesis and structural study have recently been published [5]. The crystal structure and spectroscopic study of one of the latter complexes have already been reported [6], while the study of another one is still in progress [7].

In the present paper we almost complete our investigation on Sb(III) complexes by reporting the preparation of some new ones. The IR and UV–Vis spectra of all

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complexes, and the thermal data on certain selected ones, are reported and discussed.

Experimental

C, H and N analyses were performed with a Perkin–Elmer 240 microanalyser. Infrared spectra were recorded with KBr discs on a Perkin–Elmer 467 spectrophotometer (over the range 4000–200 cm^{-1}). Electronic spectra were obtained in 1 cm quartz cells on a Perkin–Elmer/Hitachi 200 spectrophotometer. The thermoanalytical investigations were carried out with a Mettler TA 2000 system equipped with a Metrowatt SE 460 recorder. A sample weight of 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.

Benzoyl- and monochlorobenzoylhydrazones were prepared by literature methods [8].

Preparation of complexes

All these 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 its volume, affording a residue. The solid was removed by suctional filtration, washed with diethyl ether (2 × 10 ml) and dried in vacuo.

The procedure could be accomplished in considerably less time by warming the reaction mixture at 40–50°.

All the new compounds could be recrystallized from warm methanol.

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 complexes I–XV. The new compounds are microcrystalline solids, very stable in dry air. They appear to be soluble in polar solvents, e.g. ethanol, methanol, DMF and DMSO, whereas they are insoluble in the most common organic solvents. It had been anticipated that the new complexes would undergo hydrolysis [9]; indeed, they react rapidly with water, affording analogous products. Analytical results, colours and yields of I–XV are displayed in Table 1.

Table 1 Analytical and some physical data on antimony(III) complexes

Compound		Yield	Colour	C, %		H, %		N, %		X(Cl, Br, I)[a], %	
				calc.	found	calc.	found	calc.	found	calc.	found
$SbCl_3 \cdot FBHH$	I	75	white	32.56	32.40	2.26	2.25	6.33	6.30	24.08	23.99
$SbCl_3 \cdot FoClBHH$	II	70	white	30.20	30.04	1.89	1.92	5.87	5.63	22.34	22.25
$SbCl_3 \cdot FmClBHH$	III	68	white	30.20	30.06	1.89	2.05	5.87	5.87	22.34	22.29
$SbCl_3 \cdot FpClBHH$	IV	85	white	30.20	29.95	1.89	1.97	5.87	5.54	22.34	22.20
$SbBr_3 \cdot FpClBHH$	V	33	yellow	23.61	23.50	1.48	1.45	4.59	4.51	39.30	39.10
$SbI_3 \cdot FpClBHH$	VI	30	brown	19.18	19.27	1.20	1.15	3.73	3.63	50.70	50.55
$SbCl_3 \cdot TBHH$	VII	70	yellow	32.56	32.41	2.26	2.25	6.33	6.20	23.24	23.20
$SbCl_3 \cdot ToClBHH$	VIII	56	yellow	29.22	29.31	1.83	1.87	5.68	5.57	21.60	21.50
$SbCl_3 \cdot TmClBHH$	IX	50	yellow	29.22	29.25	1.83	1.88	5.68	5.56	21.61	21.44
$SbCl_3 \cdot TpClBHH$	X	51	yellow	29.22	29.59	1.83	1.90	5.68	5.60	21.61	21.57
$SbBr_3 \cdot TpClBHH$	XI	33	yellow	23.00	22.95	1.44.	1.43	4.47	4.40	38.30	38.21
$SbI_3 \cdot TpClBHH$	XII	39	brown	18.78	18.80	1.17	1.17	3.65	3.64	49.64	49.60
$SbCl_3 \cdot PmClBHH$	XIII	30	deep-blue	30.27	30.15	2.10	2.18	8.83	8.70	22.39	22.10
$SbBr_3 \cdot PmClBHH$	XIV	28	deep-blue	23.65	23.55	1.64	1.58	6.90	6.72	39.37	39.00
$SbI_3 \cdot PmClBHH$	XV	37	deep-blue	19.20	19.46	1.33	1.33	5.60	5.49	50.76	50.55

[a] The values refer to the halogen attached directly to antimony.

The conductance data on all complexes in methanol solution indicate the presence of non-electrolytes.

Electronic-infrared spectra

The absorption maxima of the studied complexes in methanol solution are listed in Table 2. The two intense absorption bands in the ranges 220–241 and 307–325 nm are due to intraligand transitions of $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ types, located mainly on the $C = N$ and $C = O$ groups, respectively [10]. No appreciable shifts were observed when the spectra of the complexes were compared with those of the free ligand. Consequently, we cannot rely on the electronic spectra in order to draw conclusions concerning the possible coordination sites of the ligands. Bands occurring in the region 480–580 nm for complexes VI and XIII–XV may be assigned to ligand-to-metal charge-transfer transitions, which are considered responsible for the colour of the compounds. However, the IR spectra are more informative about the possible coordination sites of the investigated ligands and of the others incorporated in complexes I–XV. In particular, the IR spectra of the compounds show bands due to $v(C = O)$ at lower frequencies than those of the free ligands [11–13]. The lowering lies between 15 and 75 cm^{-1}, indicating that the $C = O$ group is one of the coordination sites of the ligands. The absorption bands attributed to the $\diagdown C = N$ stretching frequency in pure hydrazones shifted to values lower by 15 to 65 cm^{-1}, indicating that the nitrogen of the azomethine moiety is the second coordination site [11–14]. The existence of bands assigned to $v(Sb–O)$ (Table 2) and to $v(Sb–N)$ lends further support to the above arguments [11–17]. Moreover, the new complexes show peaks due to $v(Sb–X)$ ($X = $ Cl, Br, I) [12, 13, 17, 18], along with bands at around 920 cm^{-1} assignable to $v(N–N)$, which are shifted to higher frequencies than those of the free ligands [19, 20]. Another feature of the IR spectra is that they exhibit bands in the range 3300–3140 cm^{-1}, indicating the presence of the $\diagdown N–H$ group in the complexed molecules [9–11]. Taking into account only the above IR data and the analytical results on all the complexes, one can presume their pseudooctahedral structure. However, the existence of bands in the region 375–345 cm^{-1} in the IR spectra of VII–XII, which can be assigned to $v(Sb–S)$, is an indication that the ligands may offer the heteroatom (O, N, S) of the heterocyclic ring as a third coordination site. Unfortunately, we have been unable to detect bands due to $v(Sb–O)$ and $v(Sb–N)$ in the spectra of the other complexes, the reason probably being either that they are obscured by related absorptions or we cannot be certain about their positions. Considering the known tendency of antimony(III) to

Table 2 The most relevant infrared and UV-Vis bands of the new antimony(III) complexes

Compound	Infrared bands (cm^{-1})						UV–Vis bands in nm (log ϵ)
	ν(C=O)	ν(N–N)	ν(Sb–N)	ν(Sb–O)	ν(Sb–X)	ν(Sb–S)	
I	1630vs^a	940s	545m	430m, 460w	340m, 320s		230sh, 310 (4.55)
II	1630vs	942s	570m	445m, 470m	340m, 320s		232 (4.19), 307 (4.53)
III	1620s	940s	550m	430m, 490m	340m, 320s		240 (4.29), 315 (4.60)
IV	1630vs	945s	545m	430w, 480w	330m, 305s		236 (4.19), 312 (4.53)
V	1635vs	940s	520m	460m, 480m	290m		241 (4.51), 311 (4.72)
VI	1630vs	940s	575w	415w, 510w	—		220 (4.80), 272 (4.76), 320 (4.57), 500sh
VII	1600vs	940w	545m	420m	335s, 310s	360w	235sh, 267 (4.25), 317 (4.58)
VIII	1600vs	950w	560w	435m	320s, 310s	350w	238sh, 273 (4.27), 323 (4.47)
IX	1610vs	930w	555w	430w	320s, 310s	375s	235sh, 271 (4.38), 320 (4.46)
X	1600vs	930w	530m	420m	320s, 310s	360s	242 (4.32), 265 (4.32), 318 (4.70)
XI	1590vs	925w	500w	415w	290w	355m	2.41sh, 268 (4.44), 318 (4.53)
XII	1580vs	925w	530w	415w	—	345m	220 (4.83), 270 (4.90), 318 (4.52)
XIII	1610s	920w	500w	420w	330w	—	235sh, 270 (4.91), 320 (3.76), 485 (3.64), 562 (3.68)
XIV	1610s	920w	520w	415w	295w	—	271 (4.74), 3.25 (3.87), 486 (3.70), 565 (3.79)
XV	1605s	920w	530w	420w	—	—	268 (4.38), 315 (4.34), 480 (3.70), 580 (3.86)

^{a} vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

achieve hexacoordination in its complexes [11], we can conclude that the new compounds may have a distorted octahedral structure.

Thermal analysis

TG, DTG and DTA curves for selected antimony(III) complexes of mono-chlorobenzoylhydrazones are shown in Figs 1–5. Detailed TG, DTG and DTA for the same complexes, and corresponding temperature ranges, mass losses and residue masses, are listed in Table 3.
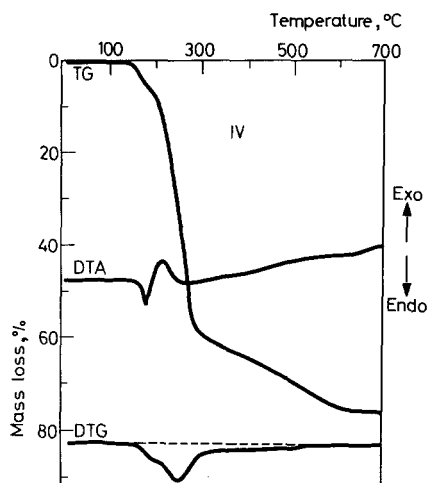

Fig. 1 Thermoanalytical curves for $SbCl_3 \cdot FpClBHH$

Generally, the thermal decompositions of the investigated complexes proceed via one or three stages; the number of such stages depends on the natures of the hydrazone and of the halogen involved.

A common feature of the thermoanalytical curves is that the DTA curves exhibit peaks at lower temperatures than those at which the TG profiles indicate the beginning of the actual mass loss. This abnormality could be rationalized by accepting that the complexes absorb energy prior to the starting of the decomposition, which is used to cause excitations and possible rearrangements of certain bonds, the rupture of which occurs at higher temperatures. Moreover, none of the DTA curves of the complexes show any peak corresponding to the main decomposition; this could be due to concomitant exothermic and endothermic reactions, each of them diminishing the effect of the other.

The TG profile of $SbCl_3 \cdot FpClBHH$ shows three consecutive steps. The first step corresponds to the evolution of a chlorine atom, whereas the second and the third

Table 3 DTA/TG/DTG data on Sb(III) complexes

Compound	DTA results Peak temperature, °C, endoth. (−) exoth. (+)	Stage	TG/DTG results Temperature range, °C	DTG$_{max}$, °C	Mass loss, %	Evolved moiety formula	Mass calculated, %
p-ClC$_6$H$_4$CONHN=CH—[furan,O] · SbCl$_3$	190 (−)	a	145–195	190	6.5	Cl	7.44
	223 (+)	b	195–292	255	50.8	{p-ClC$_6$H$_4$CONHN=CH—[furan]O}	52.16
		c	292–610		17.7	2Cl	14.87
					25.0	Sb	25.54
		residue					
p-ClC$_6$H$_4$CONHN=CH—[thiophene,S] · SbCl$_3$	197.5 (−)	a	230–410	331	83.5	{p-ClC$_6$H$_5$CONHN=CH—[thiophene]+3Cl}	75.29
		residue			16.5	?	24.70
p-ClC$_6$H$_4$CONHN=CH—[thiophene,S] · SbBr$_3$	192.5 (−)	a	190–390	315	80.8	{p-ClC$_6$H$_5$CONHN=CH—[thiophene]+3Br}	80.54
		residue		355	19.2	Sb	19.44
p-ClC$_6$H$_4$CONHN=CH—[thiophene,S] · SbI$_3$	190 (−)	a	172–345	305	70.0	{p-ClC$_6$H$_5$CONHN=CH—[thiophene]+2I}	67.58
	315 (+)						
	480 (+)	b	345–490	458	11.6	I	16.54
	585 (+)						
	625 (+)	c	490–660		12.7	?	15.87
	652 (+)				5.7	?	
		residue				~	16.92
m-ClC$_6$H$_4$CONHN=CH—[pyrrole,NH] · SbI$_3$	248 (+)	a	137–215	177	5.9	~	16.92
	627 (−)	b	215–495	295	50.1 } 68.7	{m-ClC$_6$H$_5$CONHN=CH—[pyrrole]NH}	33.01 } 66.85
				382, 443	12.7	I	16.92
		residue	495–725		31.3	{SbI}	33.15
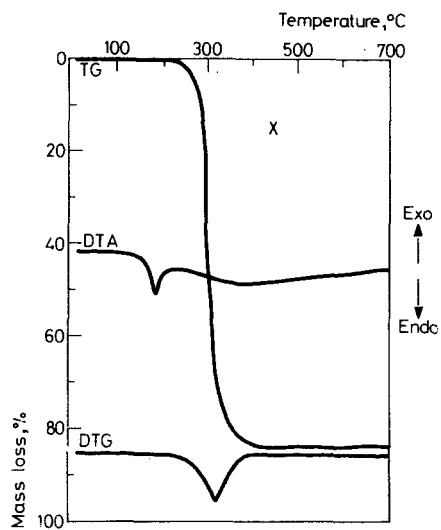
Fig. 2 Thermoanalytical curves for SbCl$_3 \cdot$ TpClBHH
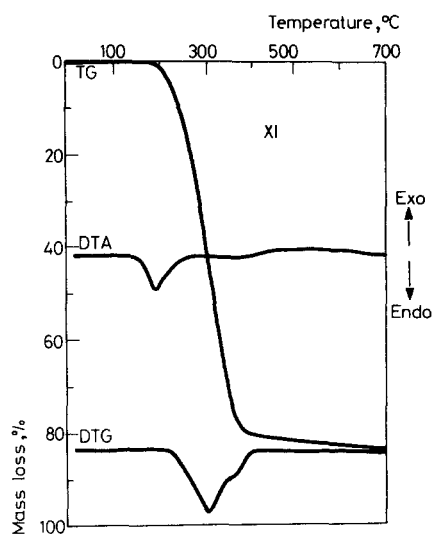
Fig. 3 Thermoanalytical curves for SbBr$_3 \cdot$ TpClBHH
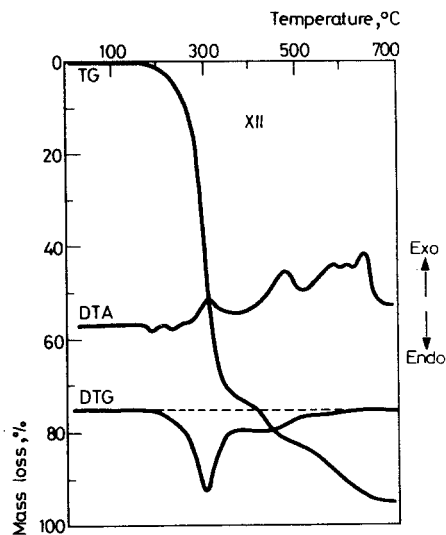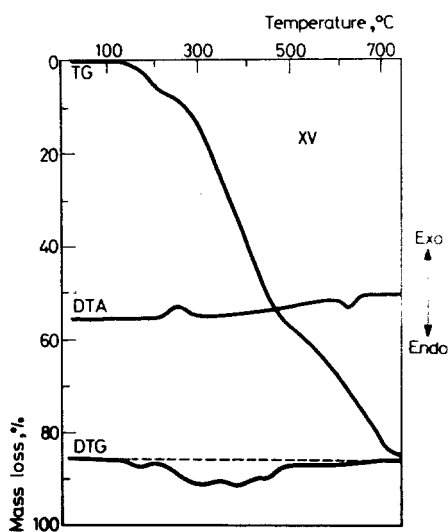
Fig. 4 Thermoanalytical curves for $SbI_3 \cdot TpClBHH$

Fig. 5 Thermoanalytical curves for $SbI_3 \cdot PmClBHH$

ones indicate the removal of the FpClBHH ligand and the loss of another 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 [21].

As far as the complexes $SbCl_3 \cdot TpClBHH$ and $SbBr_3 \cdot TpClBHH$ 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 complex shows a peak and a shoulder at 315 and 355°, respectively; the former corresponds to the loss of one ligand and a halogen, and the latter to the evolution of two halogens. The percentage of the residue left for $SbBr_3 \cdot TpClBHH$ is almost the same as the calculated one, whereas the percentage for $SbCl_3 \cdot TpClBHH$ is much lower than the expected one.

The TG curves of $SbI_3 \cdot TpClBHH$ and $SbI_3 \cdot PmClBHH$ do not display well-defined stages and their other thermoanalytical data are not very informative about their mode of degradation. In particular, the thermal decomposition of $SbI_3 \cdot TpClBHH$ appears to be rather complicated because its DTA curve contains more peaks, mainly exothermic, than the curves of all the other complexes in question. On the other hand, its TG curve suggests that it loses one ligand and two iodine atoms in one step, or one ligand and three halogens in the first two stages. The complex $SbI_3 \cdot PmClBHH$ seems to lose two iodine atoms and one ligand in three overlapping steps. The percentage of the residue left is much lower than the expected one for $SbI_3 \cdot TpClBHH$, and slightly lower for $SbCl_3 \cdot PmClBHH$.

In conclusion, the thermal investigation of the studied complexes showed that only the decomposition of $SbCl_3 \cdot FpClBHH$ proceeds in a fairly smooth and understandable way. The TG curves of the other 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 the evolved moities to escape easily, 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. A combination of the two factors may perhaps play the most important part in the decomposition of the investigated complexes.

The mass spectra in no cases exhibit 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 and the data obtained from the mass spectra, we propose the following decomposition reactions for complex IV:

$$SbCl_3(FpClBHH) \rightarrow \{SbCl_2(FpClBHH)\} + Cl \quad\quad \text{1st step}$$

$$\rightarrow \{SbCl_2\} + \{FpClBHH\} \quad\quad \text{2nd step}$$

$$\rightarrow Sb + 2Cl \quad\quad \text{3rd step}$$

Unfortunately, the available thermoanalytical data on the other studied complexes do not allow us to be sure that the above mechanism also holds for them.

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Zusammenfassung — Antimon(III)-trihalogenide, SbX_3 (X = Cl, Br und I) reagieren mit den Titelliganden und liefern Verbindungen der allgemeinen Formel SbX_3L (L = Benzoyl- bzw. Monochlorobenzoylhydrazon von 2-Furfuraldehyd (FBHH und FClBHH), von 2-Pyrrolaldehyd (PBHH und PClBHH) und von 2-Thiophenaldehyd (TBHH und TClBHH). Die neuen Verbindungen wurden mittels Elementaranalyse, Spektraldaten (IR und UV) sowie thermischen Untersuchungen beschrieben. Zwei Koordinationsstellen scheinen von den Liganden bevorzugt zu sein: die Carbonyl- und die Azomethingruppe. Eine dritte könnte das Heteroatom des heterocyclischen Ringes sein. Die thermische Zersetzung der untersuchten Komplexe vollzieht sich in Abhängigkeit von der Natur der Hydrazone und der Halogene in einem oder in drei Schritten. Als Struktur für die untersuchten Komplexe wird eine pseudo- oder verzerrte oktaedrische Struktur vorgeschlagen.

Резюме — Галоиды трехвалентной сурьмы SbX_3 (X = Cl, Br, I) реагируют с бензоил- и монохлорбензоилгидразонами фурфурола, 2-пирролальдегида и 2-тиофенальдегида, давая соединения общей формулы SbX_3L_t. Характеристика новых соединений была проведена

элементным анализом, спектроскопическими исследованиями (ИК спектроскопия и спектрос-
копия в ультрафиолетовой и видимой области), наряду с их термическим исследованием. Лиганды
предпочтительно координируются по карбонильной и азометиновой группам и, возможно,
также и по гетероатому гетероцикла. Термическое разложение комплексов протекает в одну или
две стадии в зависимости от природы обоих гидразонов и галоидов. Предложенными
структурами для комплексов являются псевдооктаэдрическая или нарушенная октаэдрическая.