Journal of Molecular Structure, 74 (1981) 255—264
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

VIBRATIONAL, NQR AND THERMOGRAVIMETRIC STUDY OF COMPLEXES BETWEEN TRIPHENYL GROUP VB COMPOUNDS AND MERCURIC HALIDES

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(Received 6 February 1981)

ABSTRACT

The synthesis, identification, vibrational (IR—FIR), NQR and thermal (TGA) study of a series of donor—acceptor complexes $(Ph_3E^{VB})_n(HgX_2)_m$ (E^{VB} = As, Sb, Bi; Ph = phenyl; X = Cl, Br, I; n/m = 2/2, 2/1) is reported. Elemental analysis proved that the aimed stoichiometry is only obtained for the $(Ph_3Sb)_n(HgI_2)_m$ and $(Ph_3As)_n(HgX_2)_m$ complexes, $(Ph_3As)_2(HgI_2)_2$ excepted. In all other cases a much lower Ph_3E^{VB} content is found. Assignments for the skeletal vibrational frequencies are based upon a "tetrahedral" C_{2v} and a "bridge-like" C_{2h} symmetry for $(Ph_3E^{VB})_2HgX_2$ and $(Ph_3E^{VB})_2(HgX_2)_2$ complexes, respectively. Changes in the electron distribution of the Hg—X bond dominate the halogen NQR frequency. TG curves are characterized by a single step mass loss and the absence of any residue suggests volatilization rather than decomposition.

INTRODUCTION

From the early work of Evans et al. [1] it appeared that mercuric halides are capable of building donor—acceptor complexes of variable stoichiometry with phosphine and arsine ligands (L), the $(L)/(HgX_2)$ ratio having the values 2/2, 2/1, 2/3, 2/4 and 3/2.

X-ray studies of mercuric halide adducts suggested an effective four-coordination of the Hg atom resulting either in a monomeric tetrahedral structure without halogen-bridging in $(Ph_3P)_2HgI_2$ [2] or in a dimeric tetrahedral arrangement with halogen-bridging in $(Et_3As)_2(HgI_2)_2$ [1] and $(Ph_3P)_2(HgCl_2)_2$ [3].

IR and FIR studies on $(R_3P)_n(HgX_2)_m$ compounds (R = Ph [4, 5], c-hexyl [6]; n/m = 2/1, 2/2) agree well with X-ray data.

The halogen [7—10] and mercury [11] NQR spectra of several mercuric halide donor—acceptor complexes with HgX_2L and HgX_2L_2 stoichiometry (L = organic O, N or S derivative) have also been studied.

In continuation of the above mentioned vibrational studies, we report an extended IR, FIR, NQR and TGA study of $(Ph_3E^{VB})_n(HgX_2)_m$ complexes (E^{VB} = As, Sb, Bi; X = Cl, Br, I; n/m = 2/1, 2/2).

EXPERIMENTAL

Synthesis

The general procedure of Evans et al. [1] for the preparation of $(R_3E^{VB})_n(HgX_2)_m$ complexes consists in mixing hot ethanolic solutions of appropriate amounts of ligand and mercuric halide. The adduct precipitates and is filtered off. In order to obtain well-defined crystalline samples (±2 mm) as required for the NQR technique, recrystallization was attempted from several solvents such as ethanol, acetone, chloroform and methylisobutylketone.

Elemental analysis

The C content was determined by combustion on a Coleman-33 carbon analyzer. Hg, As and Sb contents were measured by the non-destructive neutron activation technique, using a thermal neutron flux of 2.56×10^{12} n cm^{-2} s^{-1}. Two days after irradiation, the γ-activity was measured on a 4000-channel analyzer combined with a Ge(Li) detector. Isotopes, half-life times, γ-energies and standards used in the analysis are summarized in Table 1.

Vibrational spectroscopy

The IR spectra (4000—300 cm^{-1}) of mercuric halides, free ligands and adducts were recorded on a Perkin-Elmer IR-580 spectrometer using the Nujol-mull technique and CsI windows.

The FIR spectra (400—15 cm^{-1}) were measured with a Polytec FIR Fourier spectrometer using wig-shaped polyethylene pellets.

TABLE 1

Isotopes, half-life times, γ-energies and standards used in neutron activation analysis

Isotope	$T_{1/2}$	γ (keV)	Standard (M)
$^{196}Hg(n, \gamma)\ ^{197}Hg$	23.8 h	133.9	Phenylmercury acetate (336.74)
$^{202}Hg\ (n, \gamma)\ ^{203}Hg$	46.6 d	279.2	
$^{75}As\ (n, \gamma)\ ^{76}As$	26.3 h	559.1 657	Arsenazo (614.27)
$^{121}Sb\ (n, \gamma)\ ^{122}Sb$	2.72 d	564.1 692.5	Antimony potassium tartrate (333.927)

Thermogravimetric analysis

The TG curves were recorded on a Du Pont-950 thermogravimetric analyzer in a N_2-atmosphere using 15 mg samples. A heating rate of 15°C min^{-1} was applied.

NQR spectroscopy

The NQR signals were detected at room temperature with a Wilks Inc. NQR 1-A superregenerative spectrometer. The operational conditions and the frequency measurement procedure have already been described [12].

RESULTS AND DISCUSSION

Synthesis and elemental analysis

A comparison between calculated and experimental elemental analysis data (Table 2) clearly shows that the expected stoichiometry is only obtained in the $(Ph_3Sb)_n(HgI_2)_m$ and $(Ph_3As)_n(HgX_2)_m$ complexes (marked * in table), $(Ph_3As)_2(HgI_2)_2$ excepted. Indeed, for the latter elemental analysis, melting point and vibrational spectroscopy undoubtedly suggest that in spite of bringing together equimolar amounts of Ph_3As and HgI_2 one always obtained $(Ph_3As)_2HgI_2$. In all other cases, a marked discrepancy between experimental and calculated data is observed. The same applies to Ph_3Bi-complexes which were not therefore entered in the table. The deviations Δ = exp. % —calc. %, take positive values for Hg and negative ones for C and

TABLE 2

Elemental analysis and melting point data

Adduct[a]	C %		As %		Sb %		Hg %		Melting point (°C)
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	
$(Ph_3As)_2HgCl_2$*	48.9	48.6	17.0	17.7			22.7	23.2	247.6
$(Ph_3As)HgBr_2$*	44.4	44.5	15.4	15.3			20.6	20.9	202.1
$(Ph_3As)_2HgI_2$*	40.5	40.4	14.1	14.9			18.8	18.8	198.5
$(Ph_3AsHgCl_2)_2$*	37.4	37.2	13.0	13.1			34.7	33.1	255.6
$(Ph_2AsHgBr_2)_2$*	32.4	32.4	11.2	11.1			30.1	28.7	223.7
$(Ph_3AsHgI_2)_2$	28.4	40.5	9.9	14.8			26.4	19.2	198.0
$(Ph_3Sb)_2HgCl_2$	44.2	22.5			24.9	3.9	20.5	51.1	>300
$(Ph_3Sb)_2HgBr_2$	40.5	27.1			22.8	12.1	18.8	31.5	>300
$(Ph_3Sb)_2HgI_2$*	37.2	37.6			21.0	19.4	17.3	17.3	219
$(Ph_3SbHgCl_2)_2$	34.6	21.0			19.5	2.8	32.1	54.3	>300
$(Ph_3SbHgBr_2)_2$	30.3	19.2			17.1	5.2	28.1	44.2	>300
$(Ph_3SbHgI_2)_2$*	26.8	27.2			15.1	14.4	24.8	23.9	dec.

[a] Compounds marked * have expected stoichiometry.

E^{VB} elements. At first glance, the above findings could be interpreted in terms of a loss of Ph_3E^{VB} (E^{VB} = Sb, Bi) ligands during purification and recrystallization by scission of E^{VB}—Hg bonds (the stability normally decreases in the sequence As > Sb > Bi). However, a closer inspection of the (% C/% E^{VB}) ratio in the adducts clearly suggests scrambling reactions taking place between HgX_2 and stibine or bismuthine ligands as proposed by Deganello et al. [13].

Consequently, we only report on the vibrational and NQR spectra and on the thermal behaviour of the $(Ph_3Sb)_n(HgI_2)_m$ and $(Ph_3As)_n(HgX_2)_m$ compounds. A further investigation into the possibilities of isolating the other stibine and bismuthine adducts is under way.

IR and FIR spectroscopy

The observed IR and FIR frequencies are summarized in Tables 3—6. Due to the large number of normal modes, the vibrational analyses and assignments were based on the method of isolated group vibrations by separation of ligand and skeletal modes and neglecting coupling effects. Assignments of the observed ligand frequencies in the complexes were based upon comparisons with free ligand spectra [14, 15] and Whiffen's analysis [16] of halobenzenes. In Tables 3 and 4 only q^*, r^*, t^*, x^*, u^* and y^* E^{VB}-sensitive phenyl modes have been listed. A drop of about 20 cm^{-1} is observed on substituting As for Sb. These findings seem quite normal taking into account the appreciable vibrational amplitude impairment of the E^{VB} substituent in these six phenyl normal modes [16]. Furthermore, the stoichiometry of the complex has practically no influence on these vibrational modes.

TABLE 3

IR—FIR frequencies (cm^{-1}) assigned to vibrations of the Ph_3As moiety in $(Ph_3As)_n(HgX_2)_m$ adducts

Assignment	Ph_3As	X = Cl; *n/m* = 2/1	X = Br; *n/m* = 2/1	X = I; *n/m* = 2/1	X = Cl; *n/m* = 2/2	X = Br; *n/m* = 2/2
q^*	1081m	1081sh	1081sh	1081sh	1083sh	
	1073s	1078s	1078s	1079s	1080s	1079s
r^*	668m	670sh	682sh	682sh	675sh	675sh
y^*	475s	475s	482m	481m	470s	
	468s	468sh	472s	471s	465s	460vs
		464s	466vs	463vs	455s	
		455s	449m	449m		
t^*	325w,sh	340m	336sh	335m	347m	
	315s	328s	330s,br	328s	324s	332s
	311s	320sh	316s	315m	326s	
u^*	244m,br	241s,br	243w	244w,br	240w	240m,br
x^*	191m	205w	178sh	207w,br	207m,sh	197sh
	181sh	180w,br	170s	178w,br	178s,br	178m

TABLE 4

IR—FIR frequencies (cm^{-1}) assigned to vibrations of the Ph_3Sb moiety in $(Ph_3Sb)_n(HgI_2)_m$ adducts

Assignment	Ph_3Sb	$n/m = 2/1$	$n/m = 2/2$
q^*	1064s	1065s	1065s
r^*	654m	651w	655vw
y^*	465sh	460m	460s
	458s	458sh	450vs
	450 s	448 s	447 vs
	445sh	440sh	438sh
t^*	273s	277sh	271s,br
	269s	271vs	260s,br
	250vs	262vs	
u^*	219m	222m,br	209m
x^*	175m	181m	168s
	165m	153s	155m

TABLE 5

FIR frequencies (cm^{-1}) assigned to $E_2^{VB}HgX_2$ skeletal vibrations

Assignment[a]	As_2HgCl_2	As_2HgBr_2	As_2HgI_2	Sb_2HgI_2
ν Hg—X	287m	206m	149m	134s
ν Hg—E^{VB}	139w	142w	134s	
	100sh,br	110m	103w,br	70w,br
δ X—Hg—X	78s,br	64w,br	67w,br	54w
	70sh	50w	40m,br	74s,br
		44w,br	36m,br	

[a] ν, stretching; δ, deformation.

TABLE 6

FIR frequencies (cm^{-1}) assigned to $E^{VB}XHgX_2HgXE^{VB}$ skeletal vibrations

Assignment[a]	$AsClHgCl_2HgClAs$	$AsBrHgBr_2HgBrAs$	$SbIHgI_2HgISb$
ν_t Hg—X B_u [8, 16]	290s	201s	134s
ν_b Hg—X A_u [13]	178s,br	113m,br	69m
ν_b Hg—X	95m,br	61m,br	39m,br
B_u [17]	82m,br		36m,br
νHg—E^{VB} B_u [8, 16]	139m	130sh	52vs

[a] t, terminal; b, bridge; ν, stretching.

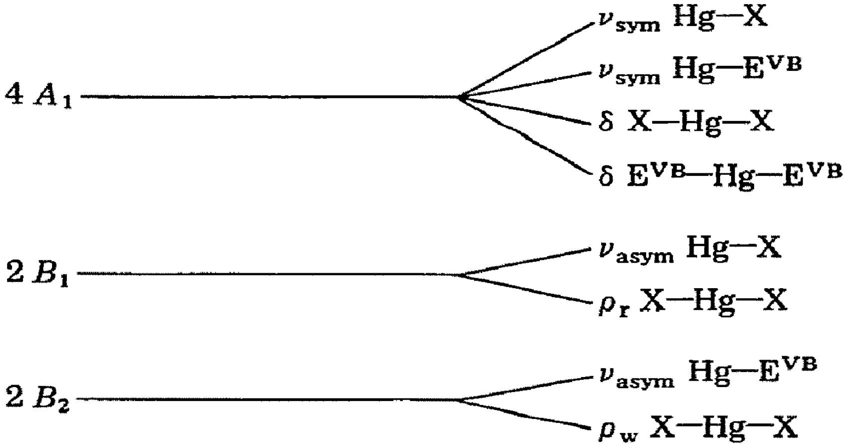
In accordance with X-ray studies on analogous mercuric adducts [2], the skeletal modes of the $(Ph_3E^{VB})_2HgX_2$-type compounds will be discussed in terms of a "tetrahedral like" C_{2v} symmetry resulting in a vibrational irreducible representation

$$\Gamma^{C_{2v}}_{vib} = 4\,A_1 + A_2 + 2\,B_1 + 2\,B_2$$

Taking into account IR-activity selection rules, the latter is transformed into

$$\Gamma^{C_{2v}}_{IR\,vib} = 4\,A_1 + 2\,B_1 + 2\,B_2$$

A correlation between C_{2v} and T_d groups shows that the 8 normal modes can be interpreted as follows

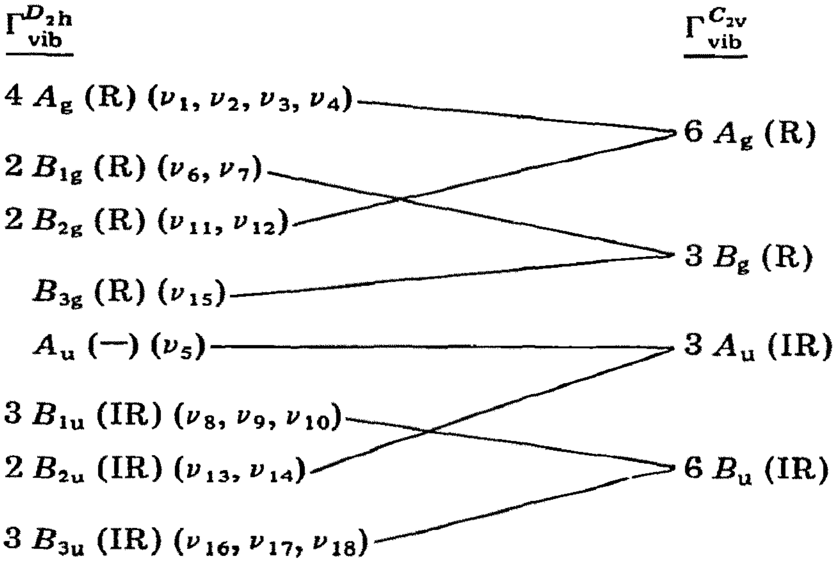


Intermolecular vibrational interactions are neglected as a consequence of the heavy mercury atom. The observed frequencies not associated with Ph_3E^{VB} ligand vibrations can thus be assigned to internal $X_2HgE_2^{VB}$ skeletal modes. Frequencies and assignments are summarized in Table 5. Several absorptions in the δ X—Hg—X region can be ascribed to solid state splitting as well as to rocking (ρ_r) and wagging (ρ_w) normal modes as observed by Nakamoto in mixed halogen compounds of the MX_2Y_2-type [17]. Finally, from Table 5 ν Hg—Br/ν Hg—Cl and ν Hg—I/ν Hg—Cl ratios of 0.72 and 0.52 respectively can be calculated. These are in good agreement with values from other analogous mercuric adducts [5, 6].

On the basis of X-ray data for analogous complexes [3], the $(Ph_3E^{VB})_2(HgX_2)_2$ complexes are presumed to have a halogen-bridged dimeric structure with *trans*-Ph_3E^{VB} ligands and a tetrahedral-like environment of the mercury atoms. Such spatial arrangement involves a C_{2h} symmetry and fits with a $\Gamma^{C_{2h}}_{vib} = 6\,A_g + 3\,A_u + 3\,B_g + 6\,B_u$ irreducible representation. In order to assign observed frequencies to local vibrations, normal coordinates are required. These can be easily found by correlation of the C_{2h} and the higher symmetry D_{2h} point groups. The irreducible representation for the D_{2h} point group is

$$\Gamma^{D_{2h}}_{vib} = 4\,A_g + A_u + 2\,B_{1g} + 3\,B_{1u} + 2\,B_{2g} + 2\,B_{2u} + B_{3g} + 3\,B_{3u}$$

The correlation between $\Gamma_{\text{vib}}^{C_{2v}}$ and $\Gamma_{\text{vib}}^{D_{2h}}$ leads to the scheme



The numbering of the fundamental frequencies used in this paper has been taken from the general work of Nakamoto [17]. From the D_{2h} normal modes and the above D_{2h}/C_{2v} correlation scheme it appears that the following vibrations especially are sensitive to halogen or E^{VB} mass effects: ν_{13} (A_u), ν_{17} (B_u) and ν_8, ν_{16} (B_u). This can be seen in Table 6.

Four sets of IR absorption bands can be recognized. One is E^{VB}-mass sensitive and the other three are X-mass sensitive. While the former is certainly to be assigned to ν Hg—E^{VB} vibrations, the latter must be ascribed to both terminal and bridging halogen—mercury vibrations. Since bridging halogen—metal vibrations normally occur at lower frequencies than terminal ones [18], the set at highest frequency must be assigned to ν_t Hg—X modes. From Table 6 it appears that two sets of IR absorptions are assigned to bridging halogen vibrations: one with A_u symmetry (ν_{13}) and one with B_u symmetry (ν_{17}). However, it has to be mentioned that only the former can be considered as a nearly pure ν_b Hg—X vibration since the ν_{17} normal mode is quite complex, explaining the lower frequency. Furthermore, the calculated ν_b Hg—X/ν_t Hg—X ratios were found to be 0.61, 0.56 and 0.51 for X = Cl, Br, I respectively and again agree well with data of other halide complexes [18].

NQR spectroscopy

In the crystal structure of the uncomplexed mercuric halides, HgX_2 (X = Cl, Br), four halogen atoms of neighbouring molecules approach the mercury atom at relatively long distances in a configuration equatorial to the X—Hg—X molecular axis. Thus each halogen atom interacts additionally with two distant mercury atoms. In 1 : 1 complexes of HgX_2 with $E^{VB}Ph_3$ (E^{VB} = P, As) two of these equatorial positions are occupied by $E^{VB}Ph_3$ units thus restricting the interactions of the halogen atoms to one distant mercury atom. In the 1 : 2 complexes all equatorial positions are occupied by $E^{VB}Ph_3$ units.

For the interpretation of the NQR data three bonding types will therefore be important: (1) the mercury—halogen σ bond; (2) the secondary mercury ··· halogen interaction; (3) the mercury—M donor—acceptor bond.

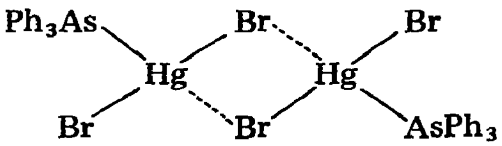
On complex formation electron density is drained towards the mercury atom so that its electrophilicity decreases and the ionic character of the Hg—X σ bond increases. According to the Townes—Dailey approximation, this results in a decrease of the halogen NQR frequency. Furthermore, due to the secondary mercury ··· halogen interactions the electron populations N_{p_x} and $N_{p_y} < 2$ in the uncomplexed mercuric halides. In 1 : 1 complexes half, and in 1 : 2 complexes all, these interactions are cancelled, raising the halogen NQR frequency. So changes in the ionicity of the Hg—X σ bond will compete with alterations in the secondary mercury ··· halogen interactions in determining the halogen NQR frequency. The experimental data (Table 7) show a net decrease of the halogen NQR frequency on complexation. Clearly the change in the ionic character of the Hg—X σ bond is the dominating factor and emphasizes the importance of the $Ph_3E^{VB} \rightarrow HgX_2$ electron donation. Nevertheless the contribution to the ν_X of secondary Hg ··· X interactions can not be neglected. This is evidenced by the fact that the $\nu^{81}Br$ in $(Ph_3As)_2HgBr_2$ (structure II) is markedly higher than in $(Ph_3AsHgBr_2)_2$ (structure I).

TABLE 7

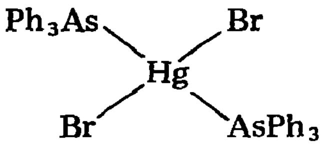
NQR data for $(Ph_3E^{VB})_2HgX_2$ and $(Ph_3E^{VB}HgX_2)_2$ at 293 K

Compound	Frequency (MHz)	*S/N*	Nucleus
$(Ph_3As)_2HgBr_2$	100.35 ± 0.03	3	^{75}As
	101.96 ± 0.03	3	
	120.11 ± 0.03	2	^{81}Br
	121.56 ± 0.03	2	
$(Ph_3As)_2HgI_2$	100.39 ± 0.03	6	^{75}As
	101.91 ± 0.03	6	
	120.29 ± 0.03	4	^{127}I (±1/2 ↔ ±3/2)
	121.95 ± 0.03	4	
$(Ph_3AsHgBr_2)_2$	116.69 ± 0.03	3	^{81}Br
$(Ph_3PHgBr_2)_2$	111.77 ± 0.03	3.5	^{81}Br
	112.83 ± 0.03	3.5	
$HgBr_2$[a]	128.43		^{81}Br
	129.38		
HgI_2[b] (yellow)	159.95		^{127}I (±1/2 ↔ ±3/2)
	161.82		

[a]See ref. 19. [b]See ref. 8.



structure I



structure II

Thermogravimetric analysis

The TG curves of all compounds in which either the $(Ph_3E^{VB})_2HgX_2$ or the $(Ph_3E^{VB})_2(HgX)_2$ stoichiometry was obtained, show the general characteristic that all mass-loss takes place in a single step. This is clearly illustrated in Figs. 1 and 2. However, $(Ph_3As)_2HgCl_2$ samples recrystallized from $CHCl_3$, lost about 4.5% of their mass between 65°C and 105°C due to the presence of $CHCl_3$ (Fig. 1A). Furthermore, all mercuric-adducts showed complete

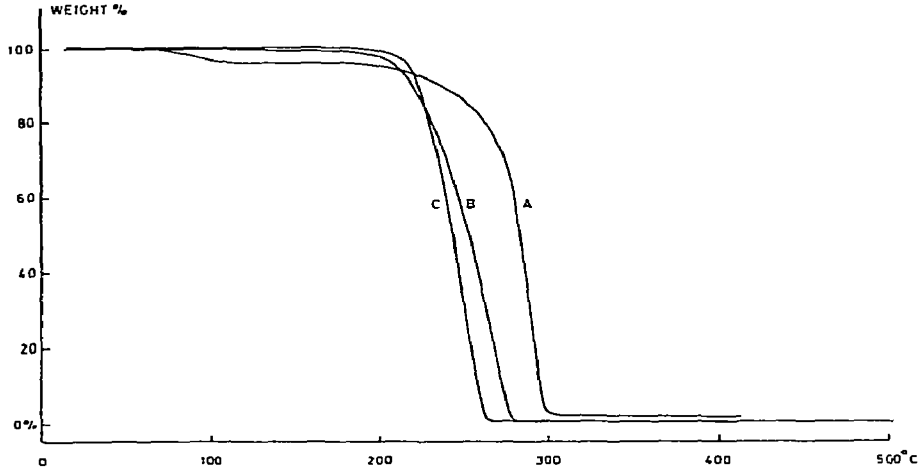


Fig. 1. TGA of $(Ph_3As)_2HgX_2$ compounds (A, X = Cl; B, X = Br; C, X = I).

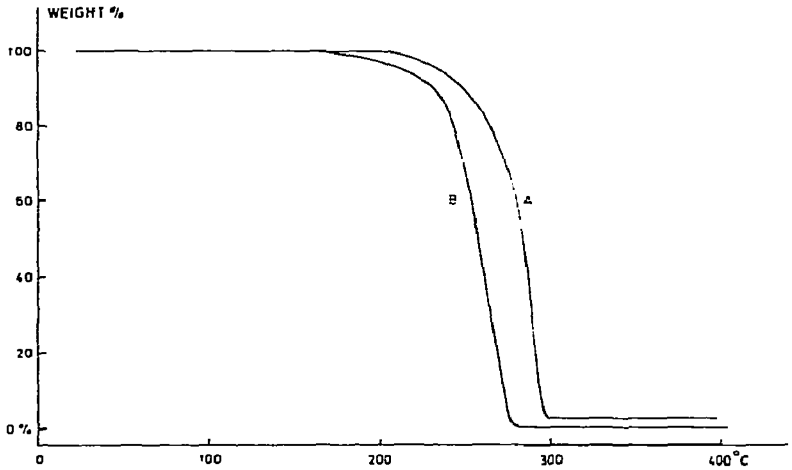


Fig. 2. TGA of $(Ph_3AsHgX_2)_2$ compounds (A, X = Cl; B, X = Br).

mass-loss between 200°C and 300°C. The lack of any residue beyond 300°C may indicate complete volatilization of the complexes without decomposition. Analogous observations have been reported for thermal decomposition studies of platinum(II) phosphine dihalide complexes [20].

ACKNOWLEDGEMENTS

The authors are indebted to Mr. T. Haemers for recording the IR—FIR spectra and to Dr. R. Dams of the analytical chemistry department for the neutron activation analysis.

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