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Molecular Complexes of Triphenylphosphine Oxide and Triphenylarsine Oxide with Antimony(III) and Bismuth(III) Halides. Vibrational Spectra and Structures

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Nine new complexes are prepared ($SbBr_3 \cdot 2(C_6H_5)_3PO$, $SbI_3 \cdot 2(C_6H_5)_3PO$, $BiCl_3 \cdot 3(C_6H_5)_3PO$, $SbBr_3 \cdot 2(C_6H_5)_3AsO$, $[SbBr_2 \cdot 4(C_6H_5)_3AsO]Br$, $[SbI_2 \cdot 3(C_6H_5)_3AsO]I$, $BiCl_3 \cdot 2(C_6H_5)_3AsO$, $BiBr_3 \cdot 3(C_6H_5)_3AsO$ *and* $2BiI_3 \cdot 3(C_6H_5)_3AsO$) *and their molecular structure and the structure of the complexes* $SbCl_3 \cdot 2(C_6H_5)_3PO$, $BiBr_3 \cdot 2(C_6H_5)_3PO$, $BiI_3 \cdot 2(C_6H_5)_3PO$ *and* $SbCl_3 \cdot 2(C_6H_5)_3AsO$ *discussed on the basis of vibrational spectra. It is shown that the mean shifts of* $\nu(PO)$ *and* $\nu(AsO)$ *are proportional to the Lewis acidity and basicity of the components, taking into account the configuration and the number of ligands. The structure of the bridging halogen bonds is discussed and caution is suggested in deducing the stereochemical inactivity of the electron lone pair of antimony(III) and bismuth(III) in polynuclear complexes from crystal structure data only. The degenerate deformation vibrations of the P–O and As–O bonds in the far infrared spectra of the free oxo-bases are located and the 1050–1150* cm^{-1} *region in triphenylphosphine oxide is reassigned.*

Introduction

The Gillespie–Nyholm treatment [1] of the stereochemistry of the trivalent elements of the V the main group of the periodic table justifies the investigations of any complex of these elements with neutral electron donors such as triphenylphosphine oxide and triphenylarsine oxide. Moreover, these complexes were so far neglected. The syntheses of only five antimony and bismuth complexes with inadequate infrared data have been reported [2, 3], and the structure of one of them ($SbCl_3 \cdot 2(C_6H_5)_3AsO$), without any pertinent crystallographic data, was referred to [4].

We prepared four of the known complexes, three of them by new procedures, synthesized nine new ones and tried to discuss their stereochemistries on the basis of vibrational spectra [5].

Experimental

The preparative work was done in dry nitrogen in Schlenk tubes. The inorganic substances were *p.a.*. The oxo-bases were recrystallized several times from benzene and dried before use by azeotropic distillation with benzene. The solvents were dried over molecular sieves or by other standard methods. There was no water present in the complexes according to infrared spectra.

Physical Measurements

Molar conductivities were measured on a Konduktometer Type E 182 Metrohm Ag., Herisau, Switzerland. Infrared spectra were recorded on Perkin–Elmer 521 and Beckman IR-11 spectrophotometers. An argon laser Spectra-Physics 52, 2W and a helium–neon laser Spectra-Physics 125, 70 mW were used for exciting the Raman spectra. X-ray powder data were obtained on a Guinier–de Wolff camera (Enraf-Nonius) with CuK$\bar{\alpha}$ radiation.

Analysis

Bismuth was determined gravimetrically as phosphate. Halogens were potentiometrically determined with silver nitrate. Arsenic was determined as in ref. 6.

Preparation of the Complexes

The complexes were prepared by mixing the solutions of the halide and the oxo-base in appropriate proportions (Table I). On cooling or evaporating the solvent, the complex crystallized. $SbI_3 \cdot 2(C_6H_5)_3PO$ is the only triphenylphosphine oxide complex that was difficult to prepare. All other triphenylphosphine oxide complexes are stable with sharp melting points. Powder diffraction data show the complexes $SbCl_3 \cdot 2(C_6H_5)_3PO$ and $BiBr_3 \cdot 2(C_6H_5)_3PO$ respectively to be isomorphous with $SbBr_3 \cdot 2(C_6H_5)_3PO$ and $BiI_3 \cdot 2(C_6H_5)_3PO$ (Table II). Triphenylarsine oxide complexes as a class were more difficult to prepare. Purification was not successful with $SbBr_3 \cdot 2(C_6H_5)_3AsO$, $BiCl_3 \cdot 2(C_6H_5)_3AsO$ and $BiBr_3 \cdot 3(C_6H_5)_3AsO$. Molar conductivities are slightly higher than with triphenylphosphine oxide series, but only two of them are 1:1 electrolytes [7]. Because of the absence

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TABLE I. Analytical and Physical Data.

Complex	Reaction Solvent[a]	Molar Ratio	Colour	M.p., °C	Λ_M[b]	Analysis							
						Calcd				Found			
						M	Hal	C	H	M	Hal	C	H
$SbCl_3 \cdot 2P$[c]	b	1:1	White	159–161	1.9		13.58	55.09	3.83		13.6	55.1	4.2
$SbBr_3 \cdot 2P$	b	1:4 1:2	Cream	168–169	4.2		26.17	47.11	3.27		26.2	47.0	3.3
$SbI_3 \cdot 2P$	b[g]	1:4	Red	52–54[d]				40.81	2.83			36.8	3.1
$BiCl_3 \cdot 3P$[e]	a	1:2	White	217–219	1.8	18.19	9.27	56.35	3.91	19.2	8.3	55.4	4.2
$BiBr_3 \cdot 2P$[f]	b[g]	1:3	Cream	180–182	3.3	20.82	23.88	43.03	3.00	21.2	22.6	43.1	3.1
$BiI_3 \cdot 2P$[f]	m[g]	1:2	Orange	198–199	5.1	18.24	33.25	37.69	2.62	18.7	33.1	37.9	2.8
$SbCl_3 \cdot 2A$[h,i]			White	200–204	11.8		12.21	49.55	3.44		12.5	48.8	3.8
$SbBr_3 \cdot 2A$	b	1:2	Cream	106–118	11.9		23.88	42.96	2.98		22.3	46.1	3.5
$[SbBr_2 \cdot 4A]Br$	b	1:10	White	194–200	36.2		14.55	52.40	3.54		14.5	52.9	4.2
$[SbI_2 \cdot 3A]I$	b[g]	1:10	Brown	164–166	36.2		25.95	44.13	3.06		25.9	42.5	3.4
$BiCl_3 \cdot 2A$	x	1:2	White	103[d]	12.5	21.79	11.10	45.03	3.13	23.0	12.1	43.8	4.9
$BiBr_3 \cdot 3A$	b	1:3 1:10	White	199–211	7.8	14.77	16.96	45.80	3.18	14.0	15.1	45.9	3.4
$2BiI_3 \cdot 3A$[j]	m[g]	1:2 1:10	Red	247–249	6.6[k]	19.49	35.49	30.21	2.10	20.2	36.4	25.5	2.0

[a] b = benzene; a = acetone; m = methanol; x = mixture of benzene, methanol and CH_2Cl_2. [b] 10^{-3} *M* in $C_6H_5NO_2$ at 22 °C. [c] P: $(C_6H_5)_3PO$. [d] Decomposition. [e] $BiCl_3 \cdot 2P$ could not be obtained[3]. [f] Previously prepared from acetone[3]. [g] Hot Soxhlet extraction of the halide into the solution of oxo-base. [h] A: $(C_6H_5)_3AsO$. [i] Prepared by the method of Phillips and Tyree, Jr.[2]. [j] Calcd: As, 10.47. Found: As, 10.6. [k] 4.10^{-4} *M* in $C_6H_5NO_2$ at 22 °C.

TABLE II. Powder Diffraction Data (*d* values and relative intensities in parentheses; CuK$\bar{\alpha}$ radiation, λ = 1.5418 Å).

$SbCl_3 \cdot 2(C_6H_5)_3PO$

10.0(40), 9.3(40), 8.4(80), 8.1(20), 7.0(60), 5.3(40), 5.02(40), 4.62(100), 4.45(40), 4.21(20), 4.10(30), 3.18(20).

$SbBr_3 \cdot 2(C_6H_5)_3PO$

10.1(40), 9.4(50), 8.5(80), 8.2(30), 7.0(60), 5.3(40), 5.03(30), 4.64(100), 4.45(30), 4.22(20), 4.12(20), 3.19(10).

$BiBr \cdot 2(C_6H_5)_3PO$

12.5(80), 10.7(100), 8.6(80), 7.7(5), 7.2(5), 6.6(5), 6.2(5), 5.7(5), 5.3(5), 4.30(50), 3.80(40), 3.35(5).

$BiI_3 \cdot 2(C_6H_5)_3PO$

12.6(80), 10.9(100), 8.8(80), 7.9(5), 7.3(5), 6.7(5), 6.3(5), 5.8(5), 5.4(5), 4.35(40), 3.82(40), 3.40(5).

of ν(AsO) bands of free triphenylarsine oxide they are formulated as $[SbBr_2 \cdot 4(C_6H_5)_3AsO]Br$ and $[SbI_2 \cdot 3(C_6H_5)_3AsO]I$.

Vibrational Spectra

Triphenylphosphine oxide and triphenylarsine oxide coordinate through the oxygen atom and the significant changes in their spectra are in the P–O and As–O stretching regions [2, 8–10]. The depletion of the electron densities in the P–O and As–O bonds on coordination is opposed by the kinematic coupling of the P–O or As–O oscillators with the oxygen–metal vibration. Approximate calculations by Cotton *et al.* [10] show the ν(PO) to shift by 50 cm^{-1} to lower frequencies relative to ν(AsO) in equivalent complexes with the linear coordinative bond of the same strength. With the bent coordinative bond, the P–O or As–O frequency will be angle dependent both by kinematic effects [11] and through the differences in hybridization [12]. Analogous complexes of the same ligand should display shifts proportional to the strength of the complex bond. If there are more ligands in the complex a splitting of the bands should occur due to coupling [2] and/or inequivalence of the bonds [1]. Since the complexes are of limited solubility in inert solvents, it is not possible to take into account solid state effects.

The changes in the organic ligand spectra below 500 cm^{-1} because of different intramolecular

TABLE III. Infrared and Raman Spectra in the Stretching Region of P–O and As–O Bonds (in cm^{-1}).[a]

$(C_6H_5)_3PO$		$SbCl_3 \cdot 2P$[b]		$SbBr_3 \cdot 2P$		$SbI_3 \cdot 2P$[c]	$BiCl_3 \cdot 3P$		$BiBr_3 \cdot 2P$		$BiI_3 \cdot 2P$		
I.R.	R.	I.R.	R.	I.R.	R.	I.R.	I.R.	R	I.R.	R.	I.R.	R.	
1188vs	1185m	1136s 1129vs	1135s	1137s 1128vs	1134s	1121vs	1169s 1152s	1167m 1154w-m	1151vs 1144vs	1152m 1140w	1149s 1142s	1152s 1139m	ν(PO)
1179sh	1179sh	1184w	1188w	1184w	1188w	1185w	1181sh	1177w	1183w	1188vw	1182vw	1184w	aβ(CH)
1163m	1165w 1156w	1159w	1165w 1158w	1159w	1165w 1157w	1161w	1162sh		1162sh	1162sh	1160sh	1160m	cβ(CH)
1120s	1119w	1118s	1115sh	1117s	1114sh		1120s	1117w	1124m 1119sh	1121m 1119vw	1113sh	1119w	q (X-sens)
1093w	1092w-m	1066s	1065w-m	1064s	1062w-m	1045s	1089m	1088w	1088s 1085sh	1085 w-m	1086s 1083sh	1084w-m	q′(X-sens)
1070m	1072vw	1079m 1075m	1075sh	1076m	1074w	1068sh	1070m	1068vw	1073w	1074vw	1071m	1071w	dβ(CH)

$(C_6H_5)_3AsO$		$SbCl_3 \cdot 2A$[d]		$SbBr_3 \cdot 2A$		$[SbBr_2 \cdot 4A]Br$		$[SbI_2 \cdot 3A]I$[c]	$BiCl_3 \cdot 2A$		$BiBr_3 \cdot 3A$		$2BiI_3 \cdot 3A$		
I.R.	R.	I.R.	R.	I.R.	R.	I.R.	R.	I.R.	I.R.	R.	I.R.	R.	I.R.	R.	
880vs	876vs	824vs 808vs	820s 806m	869s 828vs	882w 865w 824w	880vw 849w 820vs	879vs 844m 818vw	813vs	840vs	859w	864m 848vs 823vs	864s 846m 823w	857vs 846vs 835vs 824vs 818vs	857m 852s 847s 837m 825s 816m	ν(AsO)
854w 841w		846m 840m	850vw 838vw	862sh 857sh				863vw 853vw			837sh				gγ(CH)

[a] Key: s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] P: $(C_6H_5)_3PO$. [c] Raman spectra could not be obtained. [d] A: $(C_6H_5)_3AsO$.

coupling upon complexation make the spectra obscure and the selection of halide vibrations uncertain. The pronounced tendency to bridging structures in antimony(III) and bismuth(III) complexes [13] and the different amount of coupling between chain units result in different spectra in solid and solution in some cases and similar in others [14]. Hence, the obvious assignments of the strong absorptions only in the metal–halogen stretching regions were made and the stereochemical arguments based on the behaviour of ν(PO) and ν(AsO).

Spectra of Complexed Oxo-bases

The P–O and As–O stretching regions are represented in Table III. Our assignment follows that of Deacon and Green [15, 16] with the exception of the bands at 1120 and 1093 cm^{-1} in triphenylphosphine oxide. The 1093 cm^{-1} band is certainly not an overtone. It is a fundamental because of its intensity in Raman and in the complex infrared spectra [15] (Figure 1). We assign it as the symmetric component (q′, a) and the 1120 cm^{-1} band as the degenerate one (q, e) of the q(X-sens) band of the monosubstituted phenyl ring (nomenclature by Whiffen [17]) split by the coupling over the phosphorus atom in the C_3 symmetry of the triphenylphosphine oxide. Such splittings were established in other predominantly X-sensitive stretching vibrations also [18–20]. The ν(PO) in triphenylphosphine oxide is not as localized [21] as is the ν(AsO) in triphenylarsine oxide [22], and some coupling with the q′ (same symmetry representation in C_3) has to be anticipated. The molecules are tetrahedral and it may be expected that the inductive effect will primarily influence the molecular bonds (discussion and references 18, 23). Hence, it is not surprising to find the q′ band perturbed to a higher degree in the more strongly bonded antimony complexes compared to the bismuth ones.

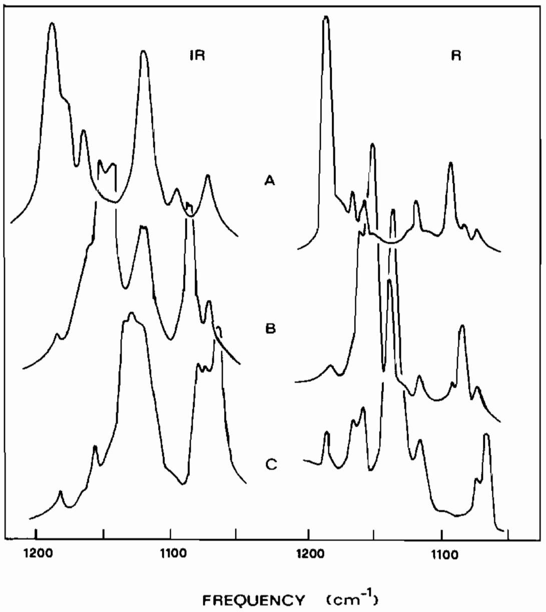

Figure 1. Representative infrared and Raman spectra of the *cis* 1:2 complexes of triphenylphosphine oxide in the stretching region of the P–O bond. A, $(C_6H_5)_3PO$; B, $BiBr_3 \cdot 2(C_6H_5)_3PO$; C, $SbCl_3 \cdot 2(C_6H_5)_3PO$.

Certain de-coupling of X-sensitive phenyl modes and the skeletal modes of the oxides below 500 cm^{-1} has to occur in proportion to the strength of oxygen coordination. Redistribution of intensities in the vicinity of t vibration in triphenylarsine oxide and three clearly defined bands in the triphenylphosphine oxide complexes in the region of t′ vibration indicate participation of the degenerate δ(AsO) and δ(PO) modes, respectively (Figure 2, Table IV) [16, 24].

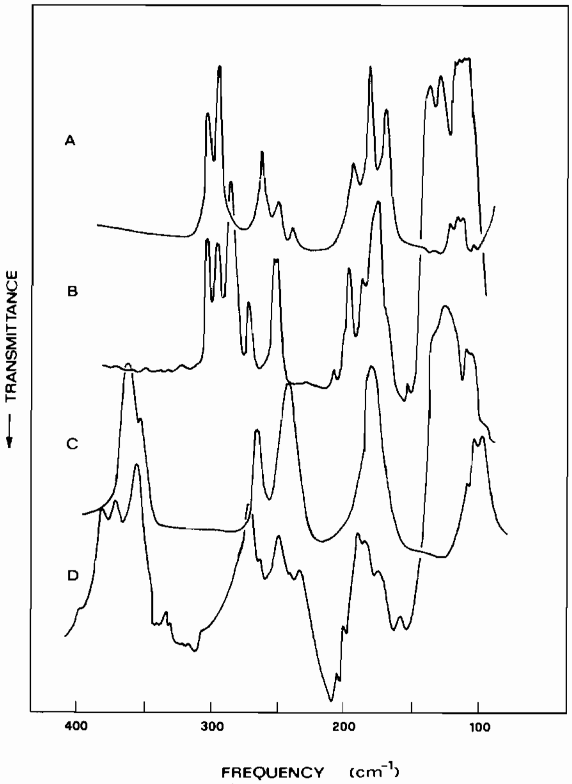

Figure 2. Perturbations in organic ligand far infrared spectra. A, $(C_6H_5)_3PO$; B, $BiI_3 \cdot 2(C_6H_5)_3PO$; C, $(C_6H_5)_3AsO$; D, $2BiI_3 \cdot 3(C_6H_5)_3AsO$.

The metal–oxygen stretching modes which should be strongly coupled with the δ(AsO) or δ(PO) modes appear around 400 cm^{-1} but are difficult to locate because of their low intensity [25, 26]. Therefore we assign this region according to Clark *et al.* [27]. No comments yet can be made about δ(PPh_3) and δ($AsPh_3$) modes, except that they should be placed below 300 cm^{-1} in both oxo-bases.

TABLE IV. Representative Far Infrared and Raman Spectra (in cm^{-1}).^{a}

SbCl$_3$·2P^b		BiBr$_3$·2P		SbCl$_3$·2A^c		BiBr$_3$·3A		
I.R.	R.	I.R.	R.	I.R.	R.	I.R.	R.	
542vs		538vs		477m-s		477s		
537vs				467m-s		471s		y (X-sens)
				463m-s	460vw	459m-s		
511m		508w						*
473m		474m		379m	371vw	367s		t (X-sens)
		455m				359s		
437m		444m		353m	352w	349s		+ δ (AsO)
	430vw	436vw						wϕ(CC)
398sh		422m	420w			418vw		+ ν(MO)^d
394w-m	390w	397w		389sh		397vw		
				328w		327vw		
				324w		324vw	321w	
308m	312w	304m		292m	293w	278m		
		296m	293w	280m		264m		t′(X-sens)
296m	296w	286m	284w	261m	268w	257m	256w	+ δ (PO)
		273vw	271w	250m	256w-m			
350m-s	346s	178m-s	178vvs	338m	337m-s	168m	165w	
		159s	152vs		321m-s	159m		
		136s				154m		ν(MHal)^e
272s	268vs	123m	127s	224s	222m-s	146m	146s	
257s	256vs			209s	206sh	135w	133s	
					184m-s			
		255w	254m	232sh	234m-s	245m	240w-m	u (X-sens)
		250sh	247m	226sh		230sh	228w-m	u′(X-sens)
196m	196s	197sh		190s		190m	190w	x (X-sens)
175w	168w-m	185sh	186vs	163m	162w		174w	+
158w	156w-m							x′(X-sens)
137m				137w				
122s	121m-s			125w	118sh	124m		Lattice
108m		102m				109w		vibr.
	99s		99s				95s	
			70vs		73vs			
			33vs		48m		45vs	

[a] Key: s, strong; m, medium; w, weak; v, very; sh, shoulder.
[b] P: (C$_6$H$_5$)$_3$PO.
[c] A: (C$_6$H$_5$)$_3$AsO
[d] M: Sb, Bi.
[e] Hal: Cl, Br.
* Combination or an overtone band [15].

Stereochemistry

The analyses, the molar conductivities of solutions in nitrobenzene and the absence of ν(PO) or ν(AsO) bands of free oxo-bases determined the formula and the coordination numbers. Mononuclear complexes, if not otherwise indicated, were presumed. Minor coupling was surmised between metal–halogen, metal–organic ligand and organic ligand vibrations because of different masses and different force constants involved [9, 10, 28].

In the molecules with two organic ligands a square pyramidal configuration, common with the 5-coordinated antimony(III) [29, 30], could be anticipated by the Gillespie–Nyholm rules [1]. Small splittings of the ν(PO) or ν(AsO) (7–16 cm^{-1}) imply equally strongly bonded ligands which excludes the apical position [1, 31] (Table III). One infrared band in SbI$_3$·2(C$_6$H$_5$)$_3$PO and BiCl$_3$·2(C$_6$H$_5$)$_3$AsO suggests a *trans* configuration with the center of symmetry in the organic ligand–metal–organic ligand segment and two bands in both infrared and Raman for SbCl$_3$·2(C$_6$H$_5$)$_3$PO, SbBr$_3$·2(C$_6$H$_5$)$_3$PO, BiI$_3$·2(C$_6$H$_5$)$_3$PO and SbCl$_3$·2(C$_6$H$_5$)$_3$AsO indicate *cis* configuration. This is in conformity with the determined crystal structures (SbCl$_3$·2(C$_6$H$_5$)$_3$AsO [4]; SbCl$_3$·2(C$_6$H$_5$)$_3$PO [32]; BiI$_3$·2(C$_6$H$_5$)$_3$PO is a binuclear complex with two bridging halogens [33]). The splitting of the highest Sb–Cl band in the Raman spectrum of SbCl$_3$·2(C$_6$H$_5$)$_3$AsO (Table IV) may be caused by solid state effects, but a more complete crystal structure determination is needed for the elucidation of the problem. The width of the bands of $BiCl_3 \cdot 2(C_6H_5)_3AsO$ (for instance the infrared bands at 840, 360 and 252 cm^{-1} have half-widths of 61, 30 and *ca.* 50 cm^{-1} respectively) suggest a polymer structure [34]. Three ν(AsO) bands in Raman are observed in $SbBr_3 \cdot 2(C_6H_5)_3AsO$. The purification was not successful and the complex may be a mixture of *cis* and *trans* isomers. There are either infrared or Raman active ν(AsO) and ν(SbBr) bands in the complex of $[SbBr_2 \cdot 4(C_6H_5)_3AsO]Br$ (Figure 3). D_{4h} symmetry with equatorially bonded organic ligands is proposed. No Raman spectrum of $[SbI_2 \cdot 3(C_6H_5)_3AsO]I$ could be obtained and we refrain from making a structure proposal. Six-coordinate complexes such as $BiCl_3 \cdot 3(C_6H_5)_3PO$ and $BiBr_3 \cdot 3(C_6H_5)_3AsO$ may have ligands in *cis* (C_{3v}) or in *trans* position (C_{2v}). There are two stretching P–O bands in triphenylphosphine oxide complex and three As–O bands in triphenylarsine oxide one, all infrared and Raman active. A similar pattern can be discerned in the metal–halogen stretching region. Hence C_{3v} symmetry is ascribed to $BiCl_3 \cdot 3(C_6H_5)_3PO$ (a_1 and e bands) and C_{2v} to $BiBr_3 \cdot 3(C_6H_5)_3AsO$ ($2a_1$ and b_2 bands). It is difficult to find an explanation for 5 infrared and 6 Raman bands in $2BiI_3 \cdot 3(C_6H_5)_3AsO$. Lazarini *et al.* [35] found a bimolecular complex with all of the triphenylarsine oxides linked to one of the bismuth atoms. There are 4 molecules in the unit cell of the $P\bar{1}$ symmetry with two molecules in an asymmetric set. There is no atom on Wyckoff's special positions and the interaction within the unit cell seems to be a correlation field effect with the sixth infrared band unresolved.

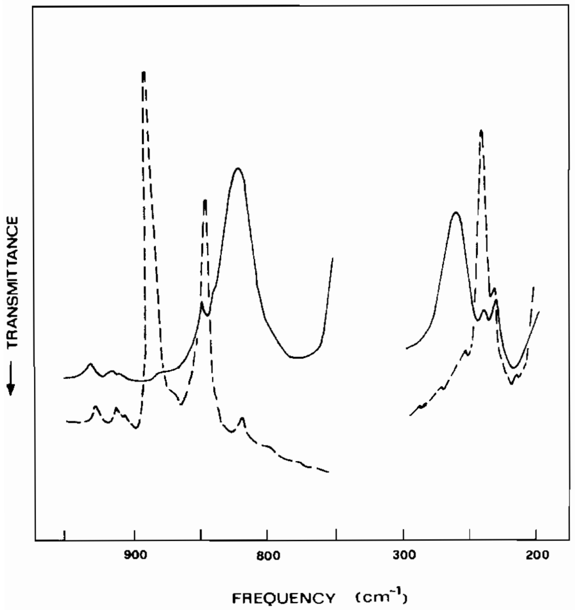

Figure 3. Infrared (——) and Raman (– – –) spectra in the stretching regions of the As–O and Sb–Br bonds of $[SbBr_2 \cdot 4(C_6H_5)_3AsO]Br$.

Conclusion

An indication of the complex bond strength can be obtained from the average negative shifts of the ν(PO) and ν(AsO) bands despite the presented variety of structures. In Figure 4 allowance is made for different kinematic couplings according to Cotton [10]. Inorganic Lewis acids are arranged by the metal electronegativities in halides, Pauling scale, calculated by the method of Huheey [36] (electron affinities and ionization potentials of antimony and bismuth were used [37]). The *trans* influence and the larger number of organic ligands should cause the weaker coordinative bonds. The three complexes with organic ligands in *trans* position in the arsine oxide series and the only one in the phosphine oxide series with three organic ligands on the central atom show significant negative deviations. Antimony(III) iodide complexes are omitted because of the absence of Raman spectra. It is obvious that the triphenylarsine oxide is a stronger Lewis base than triphenylphosphine oxide, as was also established in the case of hydrogen bonded complexes [38]. Antimony(III) halides are stronger Lewis acids than the bismuth(III) ones.

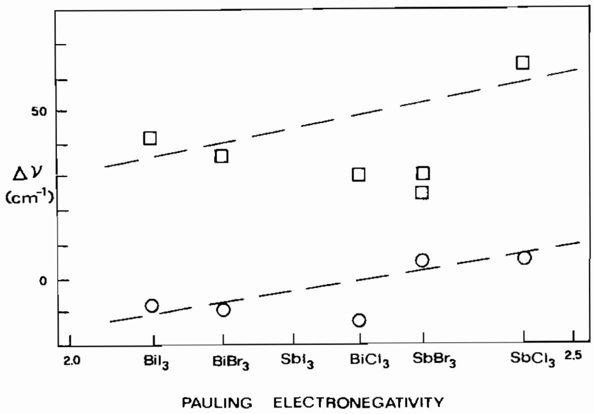

Figure 4. Mean shifts in the P–O and As–O stretching frequencies in triphenylphosphine oxide and triphenylarsine oxide upon complexation. Different kinematic couplings were assumed [10]. Inorganic Lewis acids are arranged by the metal electronegativities in their halides. ○, triphenylphosphine oxide complexes; □, triphenylarsine oxide complexes.

A four-electron three-center bond has been proposed in the mononuclear halogen complexes of antimony(III) [39]. In the polynuclear systems the halogen should be acting as a bridge by donating its free *p* electron pair to the vacant *6d* orbital of antimony with the consequent stereochemical inactivity of the antimony lone pair [40, 41]. The suggested bridge electron distribution is too crude as the easily polarisable electrons in the outer orbitals of antimony and bismuth have to take part in synergic bonding effects. The nuclear quadrupole data on bromine bridged $Sb_2Br_9^{-3}$ adduct suggest the bulging of the antimony electron kernel toward bridging bromine to a certain extent [42]. Hence it is uncautious to claim the stereochemical inactivity of the lone pair in antimony(III) and bismuth(III) binuclear or polynuclear octahedral complexes until more experimental data on electron density distribution are gathered. We can state stereochemical inactivity of the lone pair in two bismuth complexes and just one cationic antimony complex ($BiCl_3 \cdot 3(C_6H_5)_3PO$, $BiBr_3 \cdot 3(C_6H_5)_3AsO$ and $[SbBr_2 \cdot 4(C_6H_5)_3AsO]Br$) and stereochemical activity in all other studied antimony complexes, but we restrain ourselves from making any statement yet on the bismuth complexes with less than six ligands on the central atom which complete the coordination number to six by halogen bridges ($BiBr_3 \cdot 2(C_6H_5)_3PO$, $BiI_3 \cdot 2(C_6H_5)_3PO$, $2BiI_3 \cdot 3(C_6H_5)_3AsO$ and probably $BiCl_3 \cdot 2(C_6H_5)_3AsO$).

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