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ORGANOBISMUTH COMPOUNDS

X *. PREPARATION AND VIBRATIONAL SPECTRA OF COMPLEXES OF DIPHENYLBISMUTH(III) DERIVATIVES

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Summary

The cationic complex $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]^+$ and the anionic complexes $\text{Ph}_2\text{BiX}_2^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{CN}, \text{SCN}$ and N_3) have been prepared and their vibrational spectra have been investigated. The Bi—O stretching frequency for the cationic complex and the Bi—Ph and Bi—X stretching frequencies for the anionic complexes have been assigned.

Introduction

In contrast to many studies [1–4] on the acceptor properties of organometallic derivatives of Main Group IV metals, little is known about the Lewis acid behaviour of organometallic derivatives of Main Group V metals. Complexes of triorgano-antimony(V)[5] and -bismuth(V)[6] cations with some O-donor Lewis bases have been studied in this laboratory, and the anionic complexes [7] of diphenylantimony(V) halides and pseudohalides have been investigated by Bertazzi. Although preparation of the anionic complexes, $\text{Ph}_2\text{BiX}_2^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$), was reported several years ago [8], information on the nature of the bismuth—halide or bismuth—thiocyanate bonds in these complexes has been lacking. In continuation of our investigations on the skeletal vibrations [9,10] of phenyl derivatives of bismuth, we have examined the infrared and Raman spectra of the cationic complex, $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]^+$, and the anionic complexes, $\text{Ph}_2\text{BiX}_2^-$, where $\text{X} = \text{Cl}, \text{Br}, \text{CN}, \text{SCN}$ and N_3 .

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Results and discussion

Reaction of an acetone solution of diphenylbismuth(III) perchlorate with two equivalents of triphenylarsine oxide afforded the complex $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]\text{ClO}_4$. This reaction is in marked contrast with the reaction [11] of diphenylbismuth(III) chloride with pyridine which results in the formation of $\text{PhBiCl}_2(\text{Py})_2$ and Ph_3Bi . The anionic complexes, $\text{Et}_4\text{N}[\text{Ph}_2\text{BiX}_2]$, where $\text{X} = \text{Cl}$ or Br , were readily formed upon adding one equivalent of tetraethylammonium halide to an acetone solution of diphenylbismuth(III) halide. The metathetical reaction of the chloro complex, $\text{Ph}_2\text{BiCl}_2^-$, with sodium pseudohalides gave the pseudohalide complexes.

The analytical data for the complexes prepared in this work are given in Table 1. All the complexes are white crystalline solids, stable at room temperature and are unaffected by atmospheric moisture. They are insoluble in non-polar solvents but are soluble in polar solvents such as acetone and ethanol. Molar conductances for these complexes in acetone are consistent with their formulation as 1/1 electrolytes (data in Table 1).

Vibrational spectra

The infrared spectrum for the cationic complex showed strong bands at 1090 and 625 cm^{-1} due to the perchlorate ion and a strong band at 835 cm^{-1} due to the AsO stretching vibration. Since the AsO stretching frequency for free Ph_3AsO is observed at 880 cm^{-1} [12], there can be little doubt that the Ph_3AsO in the complex is coordinated to the Ph_2Bi^+ cation. In the 400 to 300 cm^{-1} region, the spectrum of the complex showed a medium-strong band at 378 cm^{-1} and a strong band at 352 cm^{-1} . The 352 cm^{-1} band is due to triphenylarsine oxide [12], and the 378 cm^{-1} band can be assigned to the Bi—O stretching frequency since no band due to either Ph_3AsO [12] or Ph_2Bi [10] moiety occurs in this region. The assignments for the As—O and Bi—O stretch-

TABLE 1
ANALYTICAL AND CONDUCTANCE DATA

Compound	M.p. ($^{\circ}\text{C}$)	Analysis (Found (calcd.)(%))			Conductance data ^a	
		C	H	N	Conc. ($10^{-3} M$)	Λ_M^b
$\text{Et}_4\text{N}[\text{Ph}_2\text{BiCl}_2]$	96	42.28 (42.56)	5.24 (5.34)	7.74 (7.74)	1.06	125
$\text{Et}_4\text{N}[\text{Ph}_2\text{BiBr}_2]$	105–108	36.43 (36.77)	4.53 (4.63)	6.83 (6.89)	1.12	130
$\text{Et}_4\text{N}[\text{Ph}_2\text{Bi}(\text{CN})_2]$	97–100	48.26 (48.42)	5.33 (5.54)	16.79 (16.98)	1.71	135
$\text{Et}_4\text{N}[\text{Ph}_2\text{Bi}(\text{SCN})_2]$	81–83 (dec.)	43.12 (43.35)	4.81 (4.96)		0.95	127
$\text{Et}_4\text{N}[\text{Ph}_2\text{Bi}(\text{N}_3)_2]$	83–85	41.86 (41.60)	5.50 (5.23)		1.07	144
$[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]\text{ClO}_4$	190	52.15 (52.07)	3.66 (3.64)		0.89	135

^a In anhydrous acetone at 25 $^{\circ}\text{C}$. ^b In $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$.

ing frequencies for the $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]^+$ cation are in complete accord with the infrared spectral data [6] for the $[\text{Ph}_3\text{Bi}(\text{OAsPh}_3)_2]^{2+}$ cation. An increase of 25 cm^{-1} in the As—O stretching frequency and a decrease of 12 cm^{-1} in the Bi—O stretching frequency in going from $[\text{Ph}_3\text{Bi}(\text{OAsPh}_3)_2]^{2+}$ to $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]^+$ are explicable in terms of differences in the oxidation states of bismuth in two complexes.

The infrared spectrum of the cyano complex showed very weak bands at 2100 and 2060 cm^{-1} due to the CN stretching vibrations [13]. For the thiocyanato complex a strong infrared band at 2030 cm^{-1} and a medium-weak infrared band at 470 cm^{-1} were observed due to the CN stretching and the NCS bending vibrations [14], respectively. The CN stretching as well as the NCS bending frequencies for the thiocyanato complex are thus indicative of the presence of N-bonded NCS ligands [14]. The infrared spectrum of the azido complex showed a very strong infrared band at 2010 cm^{-1} due to the anti-symmetric N_3 stretching frequency [15]. The assignments for the symmetric N_3 stretching frequency, the N_3 bending frequency and the CS stretching frequency are uncertain due to the presence of other bands. The CN stretching frequencies for the cyano complexes and the thiocyanato complexes are markedly lower than those observed for diphenylbismuth(III) cyanide [10] and thiocyanate [10], respectively. The antisymmetric N_3 stretching frequency for the azido complex is also significantly lower than that for diphenylbismuth(III) azide [10].

The skeletal vibrations for the anionic complexes occur in the region below 300 cm^{-1} . The observed infrared (300 to 130 cm^{-1} region) and Raman (300 to 100 cm^{-1} region) frequencies for the solid complexes together with their assignments are listed in Table 2. The observed Raman frequencies in solution (acetone) and their assignments are recorded in Table 3. Attempts to obtain the Raman spectrum of the cyano complex either in the solid state or in solution were not successful due to fluorescence and lack of sufficient solubility. The azido complex did not give a well-resolved infrared spectrum in the low frequency region.

The assignments for the skeletal vibrational frequencies for the bromo, cyano, and the azido complexes can be made with reasonable certainty. The infrared and Raman spectra for the bromo complex show a very strong band at ca. 140 cm^{-1} which is not observed for any other complex in the series. Raman measurements in acetone showed that the 142 cm^{-1} band is strongly polarized. Therefore, it is assigned to the totally symmetric Bi—Br stretching mode. The strong infrared band at 138 cm^{-1} can, therefore, be assigned to the antisymmetric Bi—Br stretching mode. The remaining infrared and Raman bands for the bromo complex are similar to those observed for other complexes; by comparison with the infrared and Raman data for the Ph_2BiX derivatives [10] it is evident that these bands are due to the skeletal vibrations of the Ph_2Bi group. The very strong polarized Raman band at ca. 200 cm^{-1} is due to the symmetric Bi—Ph stretching mode and the depolarized Raman band at ca. 210 cm^{-1} is due to the antisymmetric stretching mode. The bands at ca. 225 and 160 cm^{-1} which are observed only in the solid state are assigned to the 'u' and 'x' modes, respectively. Similarly, the strong polarized Raman bands at 280 and 205 cm^{-1} for the azido complex can be assigned to the symmetric Bi— N_3 and

TABLE 2
 FAR-INFRARED AND RAMAN SPECTRAL DATA (cm^{-1}) FOR THE $\text{Ph}_2\text{BiX}_2^-$ COMPLEXES IN THE SOLID STATE

$\text{Ph}_2\text{BiCl}_2^-$ IR	$\text{Ph}_2\text{BiBr}_2^-$		$\text{Ph}_2\text{Bi}(\text{CN})_2^-$		$\text{Ph}_2\text{Bi}(\text{NCS})_2^-$		$\text{Ph}_2\text{Bi}(\text{N}_3)_2^-$		Assignment
	Raman	IR	Raman	IR	IR	IR	Raman	Raman	
230m	230m	226m	227m	270m	222m	255s	274s	$\nu(\text{Bi}-\text{X})$	
	216s			224m			268(sh)		
	209s	208m	211s	210m	210s	212vs	209vs	u-mode	
	199m	198m	203vs	196m	198(sh)	204(sh)	206(sh)	$\nu(\text{Bi}-\text{Cl})$ $\nu(\text{Bi}-\text{Ph})$	
200s								$\nu(\text{Bi}-\text{Cl})$	
164s	160w	1385	160w	168m	160s	166w		x-mode	
			145vs					$\nu(\text{Bi}-\text{Br})$	

TABLE 3

RAMAN SPECTRAL DATA (cm^{-1}) FOR $\text{Ph}_2\text{BiCl}_2^-$, $\text{Ph}_2\text{BiBr}_2^-$, $\text{Ph}_2\text{Bi}(\text{NCS})_2^-$ AND $\text{Ph}_2\text{Bi}(\text{N}_3)_2^-$ IN SOLUTION ^a

$\text{Ph}_2\text{BiCl}_2^-$	$\text{Ph}_2\text{BiBr}_2^-$	$\text{Ph}_2\text{Bi}(\text{NCS})_2^-$	$\text{Ph}_2\text{Bi}(\text{N}_3)_2^-$	Assignment
232vs (p)		2355 (p)	280s (p)	$\nu_s(\text{Bi-X})$
202w (dp)	208w (dp)	214w (dp)	214w (dp)	$\nu_a(\text{Bi-Ph})$
212s (p)	202s (p)	208s (p)	205s (p)	$\nu_s(\text{Bi-Ph})$
	142s (p)			$\nu_s(\text{Bi-Br})$

^a In acetone. dp, depolarized; p, polarized; ν_a , antisymmetric stretching mode; ν_s , symmetric stretching mode.

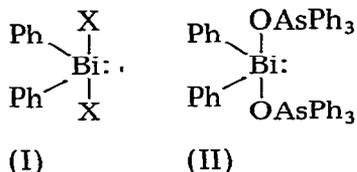
Bi-Ph stretching modes, respectively and the depolarized Raman band can be assigned to the antisymmetric Bi-Ph stretching frequency. The Raman bands at 268 and 231 cm^{-1} observed in the solid state are assigned to the antisymmetric Bi-N₃ stretching mode and the 'u' mode, respectively. The 270 cm^{-1} infrared band for the cyano complex can be assigned to the antisymmetric Bi-CN stretching frequency by comparison with the infrared and Raman data for $\text{Ph}_3\text{Bi}(\text{CN})_2$ [16]. The other infrared bands for the cyano complex are similar to those for the bromo complex and their assignments need no further comments.

The Raman spectra for the chloro and the thiocyanato complexes, in acetone, show a strong, polarized band at 232 and 235 cm^{-1} , respectively. Since these bands are not observed in the solution spectra for the bromo and the azido complexes and since no other bands attributable to the Bi-Cl or Bi-NCS stretching frequency are observed in the solution spectra, we assign the 232 cm^{-1} band to the symmetric Bi-Cl stretching frequency and the 235 cm^{-1} band to the symmetric Bi-NCS stretching frequency. The Raman spectrum of the chloro complex also shows a strong, polarized band at 212 cm^{-1} and a weak depolarized band at 202 cm^{-1} . The corresponding bands for the thiocyanato complex occur at 208 and 214 cm^{-1} . The polarized bands (212 and 208 cm^{-1}) are, therefore, assigned to the symmetric Bi-Ph stretching frequency and the depolarized bands (202 and 214 cm^{-1}) to the antisymmetric Bi-Ph stretching frequencies.

The Raman spectrum of the chloro complex, in the solid state, shows strong bands at 216 and 209 cm^{-1} , medium bands at 230 and 199 cm^{-1} and a weak band at 160 cm^{-1} . The 160 cm^{-1} band is similar to that observed for the bromo complex and can be assigned to the 'x' mode; the 209 and 199 cm^{-1} bands can be assigned to the Bi-Ph stretching modes. However, the assignments for the 230 and 216 cm^{-1} bands are not straightforward. If the 230 cm^{-1} band is due to the 'u' mode then the 216 cm^{-1} band can be assigned to the Bi-Cl stretching frequency. In that case, the chloro complex should have an associated structure in the solid state. If the aforementioned assignments are reversed, the Bi-Cl stretching frequency is not significantly altered in going from the solid state to solution and the complex can be assigned a discrete structure in the solid state. Some support for an associated structure, in the solid state, is provided by the infrared spectrum of the complex which shows a medium band at 230 cm^{-1} and a strong band at 200 cm^{-1} . Since the metal-chlorine stretching

vibrations usually give rise to stronger infrared bands than the metal-phenyl vibrations, the 200 cm^{-1} is most likely due to the Bi—Cl stretching vibration. Disappearance of the 216 cm^{-1} band and the appearance of the strong polarized band at 232 cm^{-1} in the Raman spectrum of the complex, in solution, can then be explained in terms of breaking up of the associated structure into discrete ions in going from the solid state to solution.

The discrete $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]^+$ and $\text{Ph}_2\text{BiX}_2^-$ ions are expected to have a stereochemically active lone pair. Although it is difficult to establish the structures of these ions by vibrational spectral studies, the far-infrared and Raman spectral data for the $\text{Ph}_2\text{BiX}_2^-$ ions are consistent with a distorted tetrahedral structure of C_{2v} skeletal symmetry (structure I). The observation of only one Bi—O stretching frequency in the infrared spectrum for the cation $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]^+$ is also consistent with structure II.



Experimental

General. Diphenylbismuth halides and pseudohalides were prepared as reported [10] previously. Triphenylarsine oxide was recrystallized from ethanol. Other chemicals were reagent grade and were used without further purification. Ethanol was refluxed over magnesium and distilled. Acetone was refluxed over potassium carbonate and distilled. Elemental analyses were performed by M.H.W. Laboratories, Garden City, Michigan.

Physical measurements. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Conductance measurements were made at 25°C using a Beckman RC-18 conductivity bridge. Infrared spectra were obtained with a Perkin—Elmer 180 double beam spectrophotometer using KRS-5 and polyethylene discs. The samples were prepared as mulls in Nujol and/or halocarbon oil. Raman spectra were recorded with a Spex 1400 spectrometer using the 5145 \AA excitation of an argon ion laser (Spectra Physics). The samples were sealed in glass capillary tubes. The Raman spectra in solution were measured on freshly prepared saturated solutions in acetone. The infrared and Raman frequencies are accurate to $\pm 3\text{ cm}^{-1}$.

Preparation of $[\text{Ph}_2\text{Bi}(\text{OAsPh}_3)_2]\text{ClO}_4^-$. Equimolar amounts of diphenylbismuth chloride and silver perchlorate were mixed in ethanol under an atmosphere of dry nitrogen. The mixture was stirred for an hour and then filtered. To the filtrate two equivalents of triphenylarsine oxide, was added slowly with stirring. Hexane was added to this solution to give a crystalline precipitate of the product which was filtered and dried in vacuo. Yield: 80%.

Preparation of the anionic complexes, $\text{Et}_4\text{N}(\text{Ph}_2\text{BiX}_2)$, ($X = \text{Cl}, \text{Br}, \text{CN}, \text{SCN}$ and N_3). The chloro and bromo complexes were prepared by dissolving equimolar amounts of diphenylbismuth(III) halide and tetraethylammonium halide in a minimum volume of boiling acetone. The solution was cooled to room

temperature and concentrated under vacuum. Hexane was added, dropwise, with stirring to the concentrated solution to give a white crystalline precipitate of the complex which was filtered and recrystallized from a mixture of acetone and hexane. Yield: 80–90%. The pseudohalide complexes were prepared by the metathetical reaction of the chloro complex with the appropriate sodium pseudohalide in ethanol. $\text{Et}_4\text{N}(\text{Ph}_2\text{BiCl}_2)$ (2 mmol) and the sodium salt (4 mmol) were added to ethanol (50–100 ml) and the mixture was stirred overnight in the dark, then was filtered. The filtrate was evaporated under vacuum and the resulting solid was extracted with acetone. The acetone solution was concentrated in vacuo and hexane was added dropwise, with stirring, to the concentrated solution to precipitate the complex. The product was filtered and redissolved in a minimum volume of acetone. The solution was cooled in an ice-bath and hexane was added dropwise to the cold solution to make it turbid. The turbid solution was kept cool (0°C) for several hours to give a crystalline product which was filtered and dried in vacuo. Yield: $\sim 70\%$.

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