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Synthesis and Characterization of some Arsenic, Antimony and Bismuth Complexes of 2-Mercaptoaniline

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The complexes of arsenic, antimony and bismuth as well as phenylantimony and phenylbismuth with monoanionic 2-mercaptoaniline are reported. IR spectra are consistent with chelating behaviour of the ligand but only a weak nitrogen to metal bonding interaction is advanced. The mass spectral fragmentation pattern is also presented. It can be interpreted with the loss of successive ligand units and, as a general feature, the abundance of a given ion decreases as the mass of the metal increases. Species with one or two protons less give more intense peaks possibly corresponding to ions containing the dianionic form of the ligand.

Introduction

Complexes of arsenic(III), antimony(III) and bismuth(III) with chelating ligands having S, N donor atoms, including 2-mercaptoaniline, have received very little attention. The toxicity and the air-sensitive nature of 2-mercaptoaniline itself are probably responsible for the relative neglect, in spite of the interesting dual ability in acting either as mono- or dianionic bidentate ligand [1–4]. In the latter case, where both the thio- and the amino-group are deprotonated, the coordinating behaviour of 2-mercaptoaniline appears similar to that of the unsaturated 1,2-dithiolato ligands, which have attracted considerable attention as chelating agents towards the Main Group V elements [5]. In contrast, relatively little is known about the coordinating behaviour of the same ligand in the monoanionic potentially bidentate form.

As part of a research project on the interaction of oligodentate chelating ligands with Main Group V acceptors, the synthesis and the characterization of some complexes of arsenic(III), antimony(III) and bismuth(III), as well as of phenylantimony(III) and phenylbismuth(III), with monoanionic 2-mercaptoaniline, (2-MA), has been effected, and the results are reported in this paper.

The above mentioned complexes are new compounds, except for $Bi(2\text{-}MA)_3$, previously reported but not yet characterized [6].

Experimental

Commercially available reagents and solvents were used without further purification. The salts $[Me_4N][PhSbCl_3]$ and $[NH_4][PhSbCl_5]$, used in the synthesis of the phenylantimony(III) derivative, were prepared as previously reported [7, 8].

Synthesis of the Complexes

As(2-MA)₃

To a suspension of As_2O_3 (1.0 mmol) in 20 ml of methanol, the stoichiometric amount of 2-mercaptoaniline was added under stirring and the reaction mixture gently warmed until a clear solution resulted. The yellow crystalline product obtained on cooling was recrystallized from the same solvent.

Sb(2-MA)₃ and PhSb(2-MA)₂

To a concentrated methanolic solution of SbF_3 or $[Me_4N][PhSbCl_3]$ an excess of 2-mercaptoaniline was added under stirring. The orange precipitate, obtained in both cases in a few minutes, was filtered, washed with the same solvent, and dried under reduced pressure. The monophenyl derivative was obtained by allowing a methanolic solution of $[NH_4][PhSbCl_5]$ to react with a large excess of 2-mercaptoaniline. The following reaction should occur:

$$PhSb^{V} + 2C_6H_4(SH)NH_2 \rightarrow PhSb^{III} + (SC_6H_4NH_2)_2$$

and then the solid complex is obtained as above mentioned.

Bi(2-MA)₃

$Bi_2(CO_3)_3$ suspended in methanol was treated with an excess of 2-mercaptoaniline. After stirring for

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TABLE I. Physical and Analytical Data and Molar Conductances in Methanol.

Compounds (colour)	M.p. (°C)	Analyses, found (calcd) (%)			λ_M (ohm^{-1} mol^{-1} cm^2)
		C	H	N	
As(2-MA)$_3$	115–117	48.23	4.00	9.28	6.70
		(48.31)	(4.05)	(9.39)	
Sb(2-MA)$_3$	149–151	43.80	3.73	8.54	7.21
		(43.74)	(3.67)	(8.50)	
Bi(2-MA)$_3$	165–167	36.88	2.90	7.40	8.73
		(35.94)	(3.12)	(7.23)	
$C_6H_5Sb(2\text{-}MA)_2$	157–159	48.00	3.90	6.06	6.85
		(48.34)	(3.83)	(6.26)	
$C_6H_5Bi(2\text{-}MA)_2$	198–200	40.70	3.43	5.06	7.15
		(40.45)	(3.21)	(5.24)	

TABLE II. Relevant Ions in the Mass Spectra of the Complexes.[a]

Ion	Abundance %				
X =	As	Sb	Bi	C_6H_5Sb	C_6H_5Bi
$C_6H_4(S)NH_2^+$	85	90	96	70	85
$C_6H_4(SH)NH_2^+$	100	100	100	–	90
M^+	10	22	1	8	100
MS^+	42	12	–	15	5
$C_6H_5M^+$	1	–	–	25	38
$M[C_6H_4(S)NH_2]^+$	5(95)	5(70)	2(5)	10(100)	2(22)
$M[C_6H_4(S)NH_2]_2^+$	3(15)	1(5)	–	0.5(3)	–(0.5)
$(C_6H_5)_2M^{+\bullet}$	–	–	–	15	5
$C_6H_5M[C_6H_4(S)NH_2]^+$				30(45)	3(3)
$(C_6H_5)_2M[C_6H_4(S)NH_2]^+$				22	2

[a] X = coordinating moiety. The abundance of the ions with one proton less is given parenthetically.

one hour a red crystalline solid was obtained, filtered off, washed with the same solvent, and dried under reduced pressure.

PhBi(2-MA)$_2$

Ph_3Bi was treated with an excess of 2-mercaptoaniline and the reaction mixture stirred for two hours. The solid formed was ground twice with benzene and an yellow-orange powder was obtained.

Physical and analytical data are reported in Table I. The mass spectra were obtained using a Jeol JMS-01SG-2 double focussing spectrometer, at 50 eV (75 μA). The infrared spectra of the solids were measured as nujol and halocarbon mulls in the range 4000–180 cm^{-1} using a Perkin-Elmer 580 spectrophotometer; relevant absorption bands are reported in Table III. Conductance measurements were performed on 1.0 m*M* methanolic solutions at 25 °C with a LKB 5300 B instrument; molar conductivity data are reported in Table I.

Results and Discussion

The reaction of 2-mercaptoaniline with M_2O_3 (M = As, Sb, Bi) yields trisderivatives M(2-MA)$_3$. The low solubility of the antimony and bismuth complexes in common organic solvents did not however allow recrystallization of the impure products obtained. Pure samples of Sb(2-MA)$_3$ can be easily obtained by reacting antimony trihalides with an excess of the ligand, but the same procedure failed to afford the Bi(2-MA)$_3$ derivative. In the latter case, different synthetic batches gave products with colours ranging from orange to red, having melting points in the range 80–150 °C and analytical data which did not

TABLE III. Relevant Vibrational Bands (cm^{-1}) of the Complexes in the Solid State.

$As(2\text{-}MA)_3$	$Sb(2\text{-}MA)_3$	$Bi(2\text{-}MA)_3$	$PhSb(2\text{-}MA)_2$	$PhBi(2\text{-}MA)_2$	Assignments
3470 sh		3405 w	3455 m	3455 w	$\nu(NH_2)$
3435 w,br	3425 w	3395 w	3370 w,br	3415w	
3370 w		3310 w	3340 m	3350 w,br	
3335 w,br	3330 w	3290 w	3290 w,br	3270 w	
1603 s	1600 s	1598 s	1593 s	1598 s	$\delta(NH_2)$
1305 s	1310 sh	1310 m	1312 m	1312 sh	$\nu(CN)$
	1300 s	1295 m	1298 m	1292 m	
		1290 sh	1290 sh	1285 m	
			996 m	994 m	
730 m	730 m	730 m			
			692 m	692 m	
675 mw	675 mw	675 mw	678 mw	678 mw	$\nu(CS)$
392 w	352 mw		340 m	320 m	$\nu_{as}(MS)$
360 s	355 m		320 s	305 s	$\nu_s(MS)$
275 sh	260 sh		260 sh	278 m,br	
			255 sh		
260 m,br	250 m,br		242 m,br		

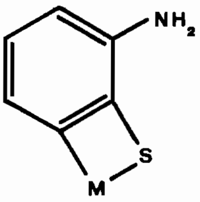
meet reasonable stoichiometries. Other salts of inorganic bismuth have been also used as reagents, including the nitrate. The dark-red compound obtained from $Bi_2(CO_3)_3$ showed the best agreement of the analytical data with the stoichiometry $Bi(2\text{-}MA)_3$. As a consequence, it appears that the orange powder, melting at 79–80 °C and previously assumed [6] as $Bi(2\text{-}MA)_3$, could be a different compound.

Solid samples of the complexes appear stable in air and insensitive to moisture over a period of weeks; the solubility in organic solvents decreases in the order As > Sb > Bi, and phenyl derivatives are less soluble than the corresponding inorganic compounds. Molar conductance data in methanol solutions indicate only a limited dissociation.

Mass Spectra

The mass spectra of $As(SC_6H_5)_3$ and $Sb(SC_6H_5)_3$, as well as that of $Sb(SC_6H_4X\text{-}p)_3$ where X = H, Me, Br, NO_2, NH_2 have been previously studied [9, 10]. The fragmentation pattern under electron impact of the monophenyl related compounds has not however been reported in the literature. Table II shows the relevant ions in the mass spectra for the present complexes. The ions corresponding to the fragmentation pattern of the ligand are not reported here, since they fully correspond to a previous report [11]. For the inorganic derivatives the free ligand constitutes the most intense signal and, as a general feature, the prominence of the peak for a given ion decreases as the mass of M increases. Possibly this is why the BiS^+ and $Bi(2\text{-}MA)_2^+$ ions have not been observed. For the phenylantimony complex, $[Sb(2\text{-}MA) - H]^+$ is the base peak and unexpectedly the ion corresponding to the free ligand is absent. The base peak for the phenylbismuth complex coresponds to the metal.

The molecular ion is always absent and the fragmentation pattern for all the complexes is consistent with the loss of successive ligand units. It is interesting to note, however, that simple bond fissions never produced the most abundant species. Peaks corresponding to ions with one or two protons less are in fact more prominent. The ion $[M(2\text{-}MA) - H]^+$ is observed for all the complexes. Plausible structures for this species are as follows:



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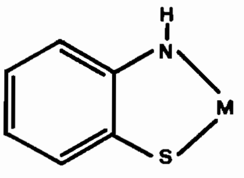

II

The ortometalation of the benzene ring has been advanced before in the interpretation of the mass spectra of some antimony and arsenic-phenoxy and thiophenoxy derivatives [9]. The structure II, which involves a five membered ring and is consistent with the known bidentate dianionic behaviour of the ligand, appears to be preferred in this case.

Among the ions not involving simple bond fission, relevant is the presence of $C_6H_5As^+$. A similar rearrangement decomposition in the phenyl complexes possibly produces the ions $(C_6H_5)_2M^+$ and $(C_6H_5)_2M(2\text{-MA})^+$.

Infrared Spectra

By a comparison of the IR spectra of the complexes with that of 2-mercaptoaniline, there is observed the absence of the broad band at 2525 cm^{-1}, attributable to the intramolecularly hydrogen-bonded thiol group. In the 3500–3200 cm^{-1} region, the solid complexes show composite IR absorptions. With the exception of the inorganic antimony derivative, in all other cases more than two bands are in fact observed because of possible chemical and crystallographic inequivalencies of the NH_2 groups. The NH_2 stretchings appear to be particularly sensitive to the nitrogen coordination, and previous assignments on complexes of 2-mercaptoaniline with transition metals [2] show a decrease of these absorptions of about 200 cm^{-1} with respect to the protonated ligand (3440 and 3350 cm^{-1}, neat liquid). Moreover, in the case of the adduct $SbCl_3 \cdot C_6H_5NH_2$, a decrease of the same order in the NH_2 stretchings has been reported [12]. The shifts found for the present compounds are considerably small and show little increase on going from arsenic to bismuth.

The IR spectra in $CHCl_3$ solution of the protonated ligand and of the complexes, excluding the phenylbismuth derivative which was almost insoluble in this solvent, have also been investigated in the NH_2 stretching region. All the spectra appear quite similar, showing two bands at 3470 and 3380 cm^{-1} and suggesting the presence of uncoordinated NH_2 groups.

A small shift at lower frequencies of the $\delta(NH_2)$ mode is observed for the solid complexes while the $\nu(CN)$ absorption appears unchanged.

The frequency of the MS stretchings follows the trend As > Sb > Bi; the intensity and resolution of the bands is also consistently decreasing in the same order. For this reason, while the values for the arsenic and antimony inorganic complexes found in the present work have been assigned and appear comparable with those observed for the corresponding thiophenoxy derivatives [9], below 400 cm^{-1} the bismuth complex shows only one weak and broad band at about 300 cm^{-1}. It therefore seems unlikely in this case to specify any particular BiS frequency. The MS bending motions are assigned to an envelope of several bands at 290–240 cm^{-1}. The complexity and the low resolution of the spectra prevent definitive evaluations of the possible contributions of MN coordination bonds, which would be predicted below 450 cm^{-1}.

The IR bands associated with the phenylantimony(III) and phenylbismuth(III) units are similar and can be interpreted in the light of previous assignments on the halophenyl metal(III) complexes [7, 13].

A discussion of the structure of the compounds described must be tentative. On the basis of infrared evidence, a chelating behaviour of the ligand can be advanced, but a weak nitrogen to metal bonding interaction appears the most reasonable hypothesis. The presence of the lone pair electrons should lead to a distorted octahedral geometry for the inorganic derivatives, while the phenyl complexes might present a pseudo-octahedral structure with the phenyl–metal bond perpendicular to the plane containing the ligands (*cf.* the X-ray structure of bis(1-oxopyridine-2-thiolato)phenylbismuth [14]). The other possibility is that the weak nitrogen-to-metal coordinative bonds do not cause considerable distortions of the bond angles (~90°) normally observed in three-coordinate arsenic(III), antimony(III) and bismuth(III) compounds.

Definite structural information on the present complexes could have been obtained from a single crystal X-ray study. In fact, the determination of the molecular structure of the arsenic derivative has been planned, but careful recrystallization work failed to give a suitable crystal.

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